

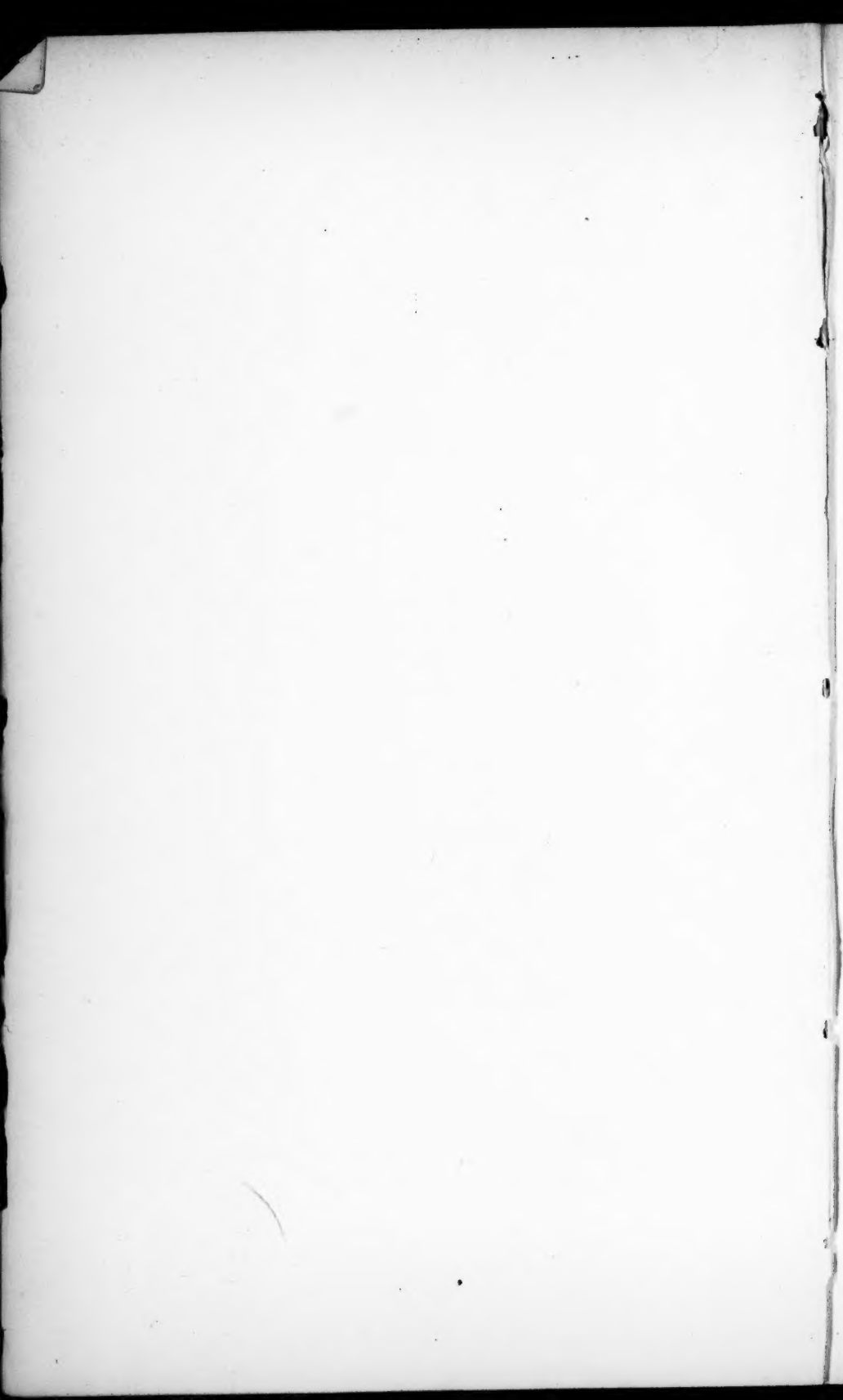
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PROCEEDINGS  
OF THE  
AMERICAN ACADEMY  
OF  
ARTS AND SCIENCES.

VOL. XVI.

PAPERS READ BEFORE THE ACADEMY.

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INVESTIGATIONS ON LIGHT AND HEAT, made and published wholly or in part with appropriation  
from the RUMFORD FUND.

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I.

DIMENSIONS OF THE FIXED STARS, WITH ESPECIAL  
REFERENCE TO BINARIES AND VARIABLES OF  
THE ALGOL TYPE.

BY EDWARD C. PICKERING.

Presented May 25, 1880.

SINCE direct measurements cannot at present be made of the disks of the fixed stars, any information with regard to their dimensions derived from the amount and character of their light will have a value. This is the course ordinarily taken in the case of a satellite or small planet, and appears to deserve a more extended trial beyond the limits of the solar system than it has yet received. The principal objection to this method is the uncertainty in the numerical value of the intrinsic brightness or other constants involved, which cannot at present be measured with accuracy. The exact formulæ will therefore be first given, and hypotheses then introduced regarding the values of these constants.

Let  $B$ ,  $b$  = the diameters of the Sun and of any given star, as seen from the Earth, expressed in seconds of arc.

Let  $l$  = the intrinsic brightness of the star, that of the sun being taken as unity; in other words, let  $l$  denote the ratio borne by the quantity of light emitted by the star to that emitted by the Sun from the same superficial area.

Let  $S, s$  = the light of the Sun and of the star expressed in stellar magnitudes by means of the scale of Pogson, in which a difference of one magnitude corresponds to the logarithmic ratio, 0.4. This ratio, expressed in numbers, is approximately 2.512.

Let  $p$  = the parallax of the star in seconds of arc.

The observed light of the star will be to that of the Sun as  $lb^2$  is to  $B^2$ ; the difference in their stellar magnitudes, or

$$s - S = 2.5 \log \frac{B^2}{lb^2} = 5 \log B - 5 \log b - 2.5 \log l.$$

Hence,  $\log b = \log B + 0.2 S - 0.2 s - 0.5 \log l.$

The radius of the Sun equals  $16' 2''$ , and accordingly  $B = 1924''$ . The value of  $S$  is more uncertain. Various determinations of the ratio of the light of the Sun to that of Sirius have been made by different observers. In 1698, Huyghens found the value 756,000,000 by reducing the light of the Sun by a minute hole.\* Wollaston, in 1829, compared the image of the Sun and of a lamp reflected in a silvered bulb of glass, and deduced the ratio 20,000,000,000.† Steinheil, in 1836, using the Moon as an intermediate standard of comparison, gave the value 3,840,000,000.‡ In 1861, Bond determined the relative light of the Sun and Moon by comparing their reflections in a glass globe with that of a Bengola light. Combining his measures with the comparisons of the Moon and Sirius by Herschel and Seidel, he deduced the value 5,970,500,000.§ In 1863, Clark found that, if the Sun was removed to 1,200,000 times its present distance and Sirius to 20 times its distance, they would appear equally bright, and equal to a sixth-magnitude star. Their ratio, consequently, equals 3,600,000,000.|| Reducing these measures to magnitudes, we obtain the values, Huyghens, 22.20; Wollaston, 25.75; Steinheil, 23.96; Bond, 24.44; and Clark, 23.89. The mean of all of these is 24.05, with an average deviation of 0.84. The last three agree well, and give 24.10, with an average deviation of 0.23. Probably 24.0 is not far from the truth, and may be assumed to represent this ratio as closely as it is at present known. If we adopt  $-1.5$  for the magnitude of Sirius, from the measures of Herschel and Seidel, we obtain for the stellar magnitude of the Sun  $-25.5$ .

\* Cosmotheoros, La Haye, 1698.

† Phil. Trans., cxix. 28.

‡ Elemente der Helligkeits-Messungen, Munich, p. 24.

§ Mem. Amer. Acad., viii. n. s., p. 298.

|| Amer. Jour. Sci., xxxvi. 76.

Substituting in the formula for  $\log b$  given above,  $B = 1924''$  and  $S = -25.5$ , we obtain  $\log b = 3.284 - 5.100 - 0.2s - 0.5 \log l = 8.184 - 0.2s - 0.5 \log l$ . This formula is exact, and would give the true diameter of any star if  $l$  was known.

An approximate value of  $l$  might be determined by the following method. Suppose that an electric current be passed through a platinum-iridium wire heating it to incandescence, and that the brightness of a short portion of it be compared with an artificial star when the current is varied by a known amount. As the current increases, the color of the light changes, the amount of the blue light increasing more rapidly than that of the red. The ratio of the two may be determined by inserting a double-image prism in the collimator of a spectroscope and viewing the wire through it. The two images may be made to overlap by any desired amount by varying the distance of the double-image prism from the slit of the collimator. The blue rays may thus be combined with the red, yellow, or green, as desired. The relative brightness of the two images may be varied by a Nicol placed in the eyepiece and turned through a known angle. We may thus combine any portion of the spectrum with any other part in such a proportion as to produce a tint to which the eye is especially sensitive. From the readings of the Nicol when different currents are passed through the wire, we may determine the varying proportion of any two rays, as the red and blue, when the wire is emitting a given amount of light. Observing in the same way the spectra of the Sun and star, and applying to them the law deduced from the observations of the wire, we obtain an approximate value of the comparative light emitted by equal areas of the two bodies. This will not be exact, since the effect of absorption is not allowed for, a difference of temperature being assumed to be the only cause of the observed difference in color. Probably the error will not be large, except perhaps in the case of the red stars. Until these measurements are made, we can do no better than to assume that  $l = 1$ , or that the emissive power is the same for the Sun and star. As a large portion of the stars have nearly the same color as the Sun, and a similar spectrum, this assumption will probably not be far from the truth. The term equivalent diameters may be conveniently applied to the quantities thus computed. They may be defined as the diameters the Sun would have if removed successively to such distances that it would equal in light stars of the given magnitudes. The expressions, equivalent densities and equivalent masses, will be used in the same manner to denote the densities or masses of bodies in their other properties resembling the Sun.

Table I. gives the equivalent diameters of stars of various magnitudes, assuming  $l = 1$ .

TABLE I. — EQUIVALENT DIAMETERS OF STARS OF VARIOUS MAGNITUDES.

Magn.	Diam.	Magn.	Diam.	Magn.	Diam.
0	0.01528	5	0.00153	10	0.00015
1	.00964	6	.00096	11	.00010
2	.00608	7	.00061	12	.00006
3	.00384	8	.00038	13	.00004
4	.00242	9	.00024	14	.00002

The diameters corresponding to the intermediate magnitudes may be found from Table II., which gives the diameters for every tenth of a magnitude from 0.0 to 4.9.

TABLE II. — EQUIVALENT DIAMETERS OF STARS FOR EACH TENTH OF A MAGNITUDE.

Magn.	Diam.	Magn.	Diam.	Magn.	Diam.	Magn.	Diam.	Magn.	Diam.
0.0	0.01528	1.0	0.00964	2.0	0.00608	3.0	0.00384	4.0	0.00242
0.1	.01459	1.1	.00920	2.1	.00581	3.1	.00366	4.1	.00231
0.2	.01393	1.2	.00879	2.2	.00555	3.2	.00350	4.2	.00221
0.3	.01330	1.3	.00840	2.3	.00530	3.3	.00334	4.3	.00211
0.4	.01271	1.4	.00802	2.4	.00506	3.4	.00319	4.4	.00201
0.5	.01213	1.5	.00766	2.5	.00483	3.5	.00305	4.5	.00192
0.6	.01159	1.6	.00731	2.6	.00461	3.6	.00291	4.6	.00184
0.7	.01107	1.7	.00698	2.7	.00441	3.7	.00278	4.7	.00175
0.8	.01057	1.8	.00667	2.8	.00421	3.8	.00266	4.8	.00168
0.9	.01009	1.9	.00637	2.9	.00402	3.9	.00254	4.9	.00160

When the magnitude is increased by five, the diameter will be reduced ten times, and the decimal point should accordingly be moved one place to the left. Thus, if a star of the 3.5 magnitude has a diameter of 0".003, one of the 8.5 magnitude will have a diameter of 0".0003 and one of the 13.5 magnitude, 0".00003. The diameter of Sirius would be that corresponding to  $-1.5$  magnitudes, or 0".03, were it not that  $l$  is probably greater than 1 owing to the blue color of the star, and the diameter consequently less.

Should future measurements render some other value of  $S$  more probable, Tables I. and II. can still be used, merely changing  $s$  by the same amount that  $S$  is altered.

The smallest star that can be seen in the 15-inch telescope of the Harvard College Observatory has a magnitude of about 15.5, and a corresponding equivalent diameter of 0".000012.



When the parallax of a star is known, these principles may be applied to determining its linear diameter. If the Sun was removed to the distance of the star its diameter would have the same ratio to the parallax that the chord of the Sun's diameter, as seen from the Earth, has to unity. It would therefore equal

$$2p \sin 16' 2'' = 0.00933p.$$

Table III. gives the light in stellar magnitudes which would be emitted by the Sun if removed to such a distance that its parallax would have the value given in the first column.

TABLE III. — PARALLAX.

Par.	Magn.	Par.	Magn.
0".1	6.07	0".6	2.18
0.2	4.57	0.7	1.84
0.3	3.68	0.8	1.56
0.4	3.06	0.9	1.30
0.5	2.58	1.0	1.07

If the parallax of  $\alpha$  Centauri is assumed to be  $0''.9$ , the Sun as seen from it will appear as a star of the 1.3 magnitude. The light of  $\alpha$  Centauri is not known with much certainty, as we have to depend upon eye estimates. Assuming the magnitude of the two components to equal 0.0 and 3.0, we find that if  $l=1$  for both of them, their diameters will be 1.82 and 0.46 times that of the Sun. The parallax of 61 Cygni may in like manner be assumed to be  $0''.3$ , and the magnitude of its components 5.0 and 6.0. The Sun would then appear, from this distance, as a star of the 3.7 magnitude, and the diameter of the two components, compared with that of the Sun, if their emissive powers are the same, will be 0.55 and 0.35.

### I. BINARY STARS.

In the case of a binary star, another equation of condition may be introduced from Kepler's third law. Let  $N$  denote the mass of the binary in terms of that of the Sun,  $P$  the period of revolution in years,  $a$  the semi-axis major, or mean distance of the components, and  $b$  the equivalent diameter, or the diameter of a star having the same mass as the binary, and the same density and intrinsic brightness as the Sun.

Comparing the binary with the system formed by the Sun and Earth seen at the same distance, we see that the two systems have masses in

the ratio of  $N$  to 1, mean distances in the proportion of  $a$  to  $p$ , and periods of revolution as  $P$  to 1. Accordingly, by Kepler's law,

$$N:1 = \frac{a^3}{P^2} : \frac{p^3}{1}, \text{ or } N = \frac{a^3}{p^3 P^2}. \text{ But } N = \frac{b^3}{(0.00933 p)^3}, \text{ since } 0.00933 p$$

will equal the diameter of the Sun at the distance of the binary. Hence, equating these two values of  $N$ ,  $p$  is eliminated, and we have  $b = 0.00933 a P^{-\frac{1}{3}}$ . The stellar magnitude corresponding to the diameter,  $b$ , may now be found from Tables I. and II. So far, no hypothesis has been introduced, and the errors in these quantities will depend only on the errors in the photometric measurements and in the micrometric determination of the elements of the orbit.

If now we could find the value of  $l$  for each of the components, as suggested above, we could determine the true diameter of the two stars, and from their orbits, and the mass of the binary, deduce their average densities. Until these measures are made, we can do no better than assume that both stars have the same density, and that  $l=1$  for each. On this hypothesis, if  $b_1, b_2$  are the equivalent diameters of the two components, and  $b$  the equivalent diameter of the binary as computed from the time of revolution and mean distance, the density will equal  $\frac{b^3}{b_1^3 + b_2^3}$ .

Since the value of the parallax is eliminated, it follows that these considerations will not aid the determination of the distance of a binary. The time of revolution of a binary would remain unchanged if removed to double the distance, provided that the linear distance of the components and their diameters were increased in the same proportion, or that the angular dimensions of the system remained unchanged. In other words, the observed time of revolution of a binary system is wholly independent of its distance from the observer.

The relative masses of the two components could be determined micrometrically and independently of the above methods, by measuring the position of each component from the adjacent stars. If this was repeated at intervals during an entire revolution of the binary, the components would be found to have described similar ellipses whose dimensions would be inversely proportioned to the masses. From the *Proc. Roy. Astron. Soc.*, xl. 235, it would appear that Mr. Gill will apply this test to the components of  $\alpha$  Centauri. If the difference in light is three magnitudes, and the intrinsic brightness and densities the same for the two components, the ratio of the masses would be as 63 to 1. The semi-axis major of the ellipse described by the larger star would therefore be, according to the elements given by Hind,

$\frac{21.80}{64} = 0''.34$ . Owing to the inclination of the plane of the orbit the apparent ellipse would be much less than this. Some other stars would appear better adapted to this test. The smaller difference in light more than compensates for the smaller orbit. From the data given in Table V., the semi-axis major of the ellipse described by several stars has been computed. The name of the star is followed by the time of revolution in years, and the semi-axis of the ellipse described by the larger component;  $\gamma$  *Coronæ Australis*, 45,  $1''.2$ ;  $\xi$  *Ursæ Majoris*, 60,  $0''.8$ ; 70 *Ophiuchi*, 94,  $0''.4$ ;  $\xi$  *Boötis*, 127,  $0''.2$ ;  $\gamma$  *Virginis*, 185,  $2''.0$ . Some others might give a larger apparent orbit, but a very long time would be required to detect the motion. When the inclination of the orbit is not zero, the apparent ellipse will be less than that computed in this manner in the same proportion that the apparent orbit is less than the real orbit described by the companion. Similar observations might be made on any double stars whose components appear to be physically connected. The proper motion, however, complicates the phenomenon, and cannot be distinguished from the orbital motion as long as the latter appears to be rectilinear.

So many large telescopes are now devoted to the measurement of double stars that there is great danger of an unnecessary duplication of work. A valuable contribution might be made to our knowledge of stellar motion by determining the positions of the components of a double star with regard to several adjacent stars. Even if the masses of the components could not thus be determined, we should at least provide the material for an accurate measurement of their proper motions in the future. The same may be said of the determination of the proper motions of other stars, which could be observed in this way with much greater precision than by the usual meridian observations. Useful work could be done by an observer unprovided with means for measurements by simply examining a large number of double stars and stars having a large proper motion, and noting the approximate position and distances of any adjacent stars near enough and bright enough for accurate measurement. A list would thus be formed from which the selection of suitable objects would be easy.

The spectroscope, which has opened so rich a field for work in astronomy, may be applied also to the study of the binary stars. If measurements could be obtained of the approach or recession of the two components, several interesting conclusions could be derived from them. A single measurement would not give the relative masses of the components, since the effect of the proper motion cannot be dis-

tinguished from that caused by the inequality of the masses. The proper motion may be eliminated if the observations are repeated in different parts of the orbit of the binary, since its effect would be always the same, while that due to the inequality of the masses would be continually altering, becoming zero and altering its sign twice during each revolution. If the ratio of the masses could be determined micrometrically as described above, the measures with the spectroscope would determine the component of the proper motion in the direction of the line of sight. The principal use of the measures with the spectroscope would be to determine the true dimensions of the orbit, and consequently the distance of the binary.

Let  $\Omega$  denote the position angle of the node of the binary,  $i$  the inclination of the plane of its true to that of its apparent orbit,  $s$  the distance, and  $p$  the position angle at the time of observation; let  $ds$  and  $dp$  represent the annual changes in these quantities. Let us make a transformation to a system of rectangular co-ordinates in which the axis of  $X$  shall coincide with the line of nodes, the axis of  $Z$  coincide with the line of sight, and the axis of  $Y$  be perpendicular to both of them. Then  $dz$  will equal the annual change in the distances of the two components from the observer, or will measure in seconds of arc the same quantity that the spectroscope measures by the difference in velocity of the two components. But

$$dz = dy \tan i \text{ and } y = s \sin (p - \Omega);$$

$$\text{hence } dz = \tan i \sin (p - \Omega) ds + s \tan i \cos (p - \Omega) dp.$$

Substituting the proper numerical values we obtain  $dz$  in seconds of arc; it should be remembered that  $dp$  must be expressed in terms of the radius, or  $57^\circ.3$  must be taken as the unit. This method may be employed if we have an ephemeris of the star, the inclination of the orbit, and the position angle of the line of nodes. If the elements of the orbit are given without an ephemeris, a different formula must be used. Let  $\rho$  denote the real distance of the components, and  $u$  the angle from the node measured in the plane of the orbit. If a system of co-ordinates is employed such that  $X'$  lies in the line of nodes,  $Y'$  perpendicular to it in the plane of the orbit, and  $Z'$  in the line of sight, we have

$$y' = \rho \sin u, \text{ and } dz' = dy' \sin i = \sin i \sin u \, d\rho + \rho \sin i \cos u \, du.$$

If the orbit is circular,  $u$  increases uniformly with the time, and  $\rho$  is constant and equals  $a$ ; hence  $dz' = a \sin i \cos u \, du$ . If in this expression  $du = \frac{2\pi}{P}$ , or denotes the fraction of the orbit

traversed in one year,  $dz' = \frac{2\pi a \sin i}{P} \cos u$ . The maximum value of this expression occurs when  $u = 0^\circ$  or  $\pi$ , and is  $\frac{2\pi a \sin i}{P}$ . If the orbit is elliptical,  $p$  and  $u$  may be deduced from the elements, and  $dz$  may be expressed as a function of the eccentricity, node, and time, multiplied by the factor, which is constant for each orbit,  $\frac{a \sin i}{P}$ .

Let  $V$  denote the velocity of light,  $v$  the velocity of approach of a star,  $\lambda$  the wave-length of a given ray of light, and  $l$  the corresponding change it undergoes, due to the velocity. Then  $V + v : V = \lambda + l : \lambda$  or  $v = V \frac{l}{\lambda}$ ;  $v$  and  $V$  are commonly expressed in kilometers per second,  $l$  and  $\lambda$  in ten-millionths of a millimeter;  $V = 300000$ . The line  $F$  is frequently used in these measures, and for it  $\lambda = 4865$ . Substituting these values,  $v = 62 l$ . For the  $D$  line,  $\lambda = 5900$ , and since the interval between the two components equals 6, a velocity of 305 kilometers per second will be required to produce a deviation equal to the interval between these lines. It will be more convenient to measure the velocity of a star in terms of  $m$ , the annual motion, taking the distance from the Earth to the Sun as a unit. This may then be reduced to seconds of arc, if the distance of the star is known, by multiplying by the parallax  $p$ . Light traverses the distance from the Earth to the Sun in about 498 seconds, or would traverse 63300 times this distance in a year. Accordingly,  $v = 63300 \frac{l}{\lambda}$ ; for the  $F$  line  $v = 13 l$ , for the interval of the  $D$  lines,  $v = 64 l$ . If  $l$  is positive or the line moves toward the red end, it denotes that the star is receding from the observer. We have thus two values of the relative motion of the stars in the line of sight; one,  $dz$ , deduced by computation from the micrometer measurements; the other,  $v p$ , or  $13 l p$ , if the  $F$  line is observed, found by the spectroscope. Equating these values, since  $p$  is the only unknown quantity,  $p = \frac{dz}{13 l}$ . The dimensions of the orbit are now found directly, since  $\frac{a}{p}$  will equal the semi-axis major in terms of the distance of the Sun from the Earth.

It not unfrequently happens that we have an estimate of the difference in magnitude of the two components of a double star by one observer using a telescope, and also an estimate of their combined light by another observer viewing them with the unassisted eye. From these data we wish to determine the brightness of either component alone. Sometimes we have the opposite problem, given the magnitude of the separate stars to find that of both, as seen by the eye or in a

telescope not capable of separating them. Let  $l$  denote the light of the fainter star in terms of the brighter, and  $m$  the magnitude of the fainter minus the magnitude of the brighter. Then, on Pogson's system,  $m = -2.5 \log l$ . If  $M$  is the magnitude of the brighter star minus that of a star equivalent to the two combined, or having the light  $(1 + l)$ , then  $M = -2.5 \log (1 + l)$ . From these formulæ we can always find the corresponding values of  $M$  and  $m$ . The maximum value of  $M = 0.75$  when  $m$  is zero or the stars are equal. Table IV. enables us to determine  $M$  to the nearest tenth of a magnitude for any value of  $m$ . As an example, suppose two stars have magnitudes 2.0 and 3.0; then  $m = 3.0 - 2.0 = 1.0$ , and  $M$ , from the table, lies between 0.35 and 0.45 or equals 0.4. The light of both combined will therefore equal  $2.0 - 0.4 = 1.6$ .

TABLE IV.—COMBINATION OF TWO STARS.

$M$ .	$m$ .	$m'$ .
0.05	3.32	1.90
0.15	2.07	1.06
0.25	1.47	0.64
0.35	1.05	0.34
0.45	0.72	0.11
0.55	0.45	—
0.65	0.22	—
0.75	0.00	—

It is sometimes convenient to know what would be the magnitude of a star whose mass was equal to that of the two components of a double star of the same density and brightness. Let  $m'$  equal the difference in magnitudes of the two components, and  $l$  and  $n$ , the light and mass of the fainter in terms of the brighter. Then

$$m' = -2.5 \log l = -2.5 \log n^3 = -1.67 \log n,$$

since the light is proportional to the square, and the mass to the cube, of the diameter. If then  $M$  equals the magnitude of the brighter component minus that of both combined, we shall have  $M = 1.67 \log (1 + n)$ , from which  $M$  is determined as before from any given value of  $m'$ . The third column of Table IV. gives the value of  $m'$  corresponding to every odd twentieth of a magnitude of  $M$ . The value of the latter may thus always be determined to the nearest tenth of a magnitude. The maximum value of  $M$  is 0.50, when  $m' = 0$ . Adopting the same magnitudes as in the last example, if two stars have the magnitudes of 2.0 and 3.0,  $m'$  will equal 1.0. This value from the third column of Table IV. will correspond to a value of  $M$  lying between 0.15 and 0.25, or will equal 0.2. The magnitude

of a star having the same mass as the binary will therefore have a magnitude  $2.0 - 0.2 = 1.8$ .

Most of the binary stars whose orbits have been computed are compared in Table V. The successive columns give a current number, the name of the star, the number of the Dorpat Catalogue, the right ascension and declination for 1880, the semi-axis major in seconds, the eccentricity, the period in years, and the inclination of the plane of the orbit in degrees. The next two columns give the magnitudes of the components as estimated by Struve. Three of the stars are not contained in the Dorpat Catalogue, and for them the magnitudes given have been assumed. The next column gives the equivalent diameter  $0.00933 \alpha P^{-\frac{1}{3}}$ , or the magnitude of a star having the mass of the binary and the density and brightness of the Sun. From the magnitudes of the components we may compute, by the third column of Table IV., the brightness of a star having the same mass as the binary and the same brightness and density as its components. Subtracting from this quantity that given in the preceding column gives the next column. If these quantities were small, we might assume that they were due to errors in the assumed magnitudes of the stars. Their variations are, however, far too large to be explained in this way. As they are almost all negative, we may infer that the assumed light of the Sun is too small, or that a larger value should have been given on page 2 to  $S$ . A great part of the difference must be ascribed to variations in the density or brightness of the stars. We have at present no way of discriminating between these causes. Such a method as has been proposed on page 3 for determining  $l$  would serve to distinguish them. Until then, it will be convenient to reduce this difference from magnitudes to the relative diameters of two stars of equal density and brightness, one having a mass, the other emitting a light equal to that of the binary. Assuming the diameter of the first of these stars as a unit, the diameter of the other is given in the next column, and may be denoted by  $C$ . In almost all cases this quantity is greater than unity, from which we should infer that most of the stars enumerated are either much brighter or much less dense than the Sun, unless, as suggested above, the measurements of the light of the Sun are largely in error. Let  $d$  denote the density,  $b$  the brightness of the components of the binary, and  $D$  the equivalent diameter of the binary in terms of the same unit as  $C$ . Then  $D^2 : C^2 = 1 : b$ , and  $D^3 : 1^3 = 1 : d$ ; eliminating  $D$ ,  $C = \frac{b^{\frac{1}{3}}}{d^{\frac{1}{3}}}$ , or the brightness is proportional to the square of  $C$  and the density inversely as its cube. If



TABLE V.—BINARY STARS.

No.	Name.	z.	R. A. 1880.	Dec. 1880.	$\alpha$	$e$	P.	i	A.	B.	Equiv. Magn.	O.—C.	Relat. Diam.	$\frac{\alpha \sin i}{P}$	Computer.
1	42 Comae Berenicens.....	1728	13 4.1	+ 18 16	0.66	0.46	25.7	90.0	6.0	6.0	6.7	1.2	1.74	0.026	O. Struve.
2	5 Herculis.....	2084	16 36.8	+ 31 49	1.36	0.41	34.6	51.1	3.0	6.5	5.5	-2.5	3.16	0.031	Flammarion.
3	Anon. Leonis.....	3121	9 10.7	+ 29 47	0.71	0.26	37.0	74.2	7.5	7.8	7.0	+0.1	0.96	0.019	Doberck.
4	7 Comae Borealis.....	1937	15 18.2	+ 30 43	0.99	0.29	40.2	60.4	5.2	5.7	6.4	+0.1	1.99	0.021	Flammarion.
5	221 B Ophiuchi.....	2173	17 24.7	- 16 32	1.01	0.13	45.4	80.5	6.2	6.1	6.6	-1.2	1.74	0.022	Dun. F.
6	a Canis Majoris.....	6	6 39.7	- 16 32	7.11	0.61	49.4	47.1	1.5	8.5	2.5	-4.0	6.31	0.106	Auwers.
7	7 Comae Australls.....	18 68.3	- 37 14	+ 32 13	2.40	0.70	55.6	68.6	4.4	5.3	5.0	0.0	1.00	0.040	Schlaparelli.
8	7 Ursae Majoris.....	11 11.8	- 32 13	+ 32 13	2.58	0.38	60.7	66.3	4.4	5.3	5.0	-0.8	1.44	0.037	Hind.
9	5 Cancri.....	18 5.3	+ 18 1	- 18 1	0.91	0.35	62.4	20.7	6.0	5.7	6.2	-2.4	3.02	0.005	O. Struve.
10	a Cancri.....	18 3.8	- 18 20	- 18 20	2.40	0.70	55.6	68.6	4.4	5.3	5.0	-0.8	1.44	0.037	Hind.
11	70 Ophiuchi.....	2272	17 59.4	+ 25 33	4.80	0.39	92.8	62.1	4.0	6.3	4.2	-0.2	1.50	0.046	Flammarion.
12	7 Comae Borealis.....	1967	15 37.7	+ 25 41	0.70	0.35	95.5	85.2	4.0	7.0	8.4	-0.2	1.50	0.046	Flammarion.
13	7 Scorpil.....	1968	15 57.8	- 11 2	1.26	0.48	95.9	68.7	4.9	5.2	7.2	-2.7	3.47	0.012	Doberck.
14	Anon. Cassiopeiae.....	3062	23 59.9	+ 57 46	1.27	0.46	104.4	32.2	6.9	8.0	7.3	-0.5	1.26	0.006	"
15	a Leonis.....	1356	9 22.0	+ 9 35	0.89	0.54	110.8	64.1	6.9	8.0	7.3	-0.5	1.26	0.006	"
16	p Eridani.....	407	3 24.3	- 11 32	3.82	0.38	117.5	44.7	8.2	10.7	8.1	-2.1	2.63	0.007	"
17	25 Canum Venaticorum.....	1708	13 52.1	+ 36 54	0.75	0.96	124.5	51.5	5.7	7.6	8.7	+3.1	0.24	0.023	"
18	8 Bootis.....	1888	14 45.8	+ 19 36	4.86	0.71	127.4	38.9	4.6	6.9	4.7	-3.1	4.17	0.005	"
19	7 Virginis.....	1670	12 56.6	- 0 47	3.39	0.87	175.0	0.0	3.0	3.0	5.9	-3.4	4.79	0.023	Flammarion.
20	7 Ophiuchi.....	2282	17 53.5	- 8 11	3.97	0.90	185.0	35.1	5.0	5.7	5.9	-3.1	4.17	0.012	Thiele.
21	7 Cancri.....	2055	16 41.8	+ 52 11	0.91	0.51	222.9	58.7	4.0	5.7	8.3	+3.3	4.57	0.005	Doberck.
22	7 Ophiuchi.....	2055	16 41.8	+ 52 11	0.91	0.51	222.9	58.7	4.0	5.7	8.3	+3.3	4.57	0.005	Doberck.
23	7 Ophiuchi.....	2055	16 41.8	+ 52 11	0.91	0.51	222.9	58.7	4.0	5.7	8.3	+3.3	4.57	0.005	Doberck.
24	7 Ophiuchi.....	2055	16 41.8	+ 52 11	0.91	0.51	222.9	58.7	4.0	5.7	8.3	+3.3	4.57	0.005	Doberck.
25	44 Bootis.....	1909	14 59.8	+ 48 47	3.09	0.71	261.1	70.1	5.2	6.2	8.7	+4.6	8.92	0.004	"
26	a <sup>2</sup> Bootis.....	1908	15 20.0	+ 37 46	3.09	0.71	261.1	70.1	5.2	6.2	8.7	+4.6	8.92	0.004	"
27	36 Andromedae.....	73	0 48.0	+ 22 58	1.47	0.90	280.3	40.0	6.7	7.3	8.4	-1.7	2.19	0.011	"
28	7 Leonis.....	1424	10 13.4	+ 20 27	1.54	0.65	349.1	41.6	6.2	7.3	8.6	-2.0	3.51	0.003	"
29	61 Cygni.....	2579	19 41.2	+ 44 50	2.31	0.29	415.1	37.7	3.0	7.9	8.0	-6.2	3.47	0.003	"
30	a Comae Borealis.....	2758	21 1.4	+ 38 7	15.40	0.75	845.9	31.9	5.1	6.0	4.0	+0.9	0.65	0.005	Behrmann.
31	32 a Comae Borealis.....	2932	16 10.2	+ 34 10	5.88	0.75	845.9	31.9	5.1	6.0	4.0	+0.9	0.65	0.005	Doberck.
32	32 a Comae Borealis.....	1110	7 27.0	+ 32 9	7.43	0.33	1001.2	44.6	2.7	3.7	7.0	-4.2	2.51	0.005	"
33	5 Aquarii.....	2509	22 22.6	- 0 0	7.64	0.65	1578.3	44.7	4.0	4.3	7.3	-3.7	6.50	0.003	"



then the star has the same density as the Sun, the square of  $C$  will give its brightness. Again, if the star has the same brightness as the Sun, its density will equal one divided by the cube of  $C$ .

The product of the semi-axis major by the sine of the inclination and divided by the period is given in the last column but one. It serves as a measure of the annual approach or recession of the two components. Neglecting the eccentricity, the maximum motion in seconds will equal this quantity multiplied by  $2\pi = 6.28$ .

The last column gives the name of the astronomer by whom the orbit was computed, which is adopted in this discussion.

An inspection of the last column but one shows that the value of  $\frac{a \sin i}{P}$  in several cases amounts to  $0''.03$  or even more. Neglecting the eccentricity, the maximum motion would therefore equal  $2\pi$  times this quantity, or nearly  $0''.2$ . The eccentricity in some cases would diminish the motion, but in other cases it would increase it. An eccentricity of  $0.5$  might vary it from  $0''.1$  to  $0''.4$ , according to the position of the peri-astron. This value of  $\frac{a \sin i}{P}$  would probably be even larger for some of the recently discovered stars, in which  $P$  is still smaller than in the stars given in the table. It is commonly supposed that the parallax of an average first-magnitude star does not much exceed  $0''.1$ . That of a sixth-magnitude star would then be about  $0''.01$  unless the fainter stars are really smaller than the brighter, or unless there is a perceptible absorption of light in space. Substituting the values  $dz = 0''.2$ ,  $p = 0''.01$ , in the formula for the  $F$  line,  $p = \frac{dz}{13l}$ , given on page 9, we deduce  $l = \frac{dz}{13p} = 1.5$ . Accordingly the difference in the positions of the  $F$  line would be  $1.5$  times as great as the deviation observed in the case of Sirius. As the spectra of the two components could be observed in turn (or perhaps simultaneously) without disturbing the spectroscope, many of the causes of uncertainty present in similar measures of single stars would be removed.

In any case, if the  $F$  line could be seen in both components, we could assign a limit within which we could be certain that it was the same for both, and this would give a value of the parallax which must be less than the true parallax. A determination of the outside limit of distance of a star would appear to have nearly the same importance as the inside limit of distance found by micrometric distance. Moreover it does not seem probable that a star will be found whose parallax is very large, or previous observation might have detected it.

The search for a star with a very small parallax seems more hopeful, since it could not have been detected by other measures.

The observation would have value if we could determine the direction of the motion, even if we could not measure its amount, since it would show which portion of the orbit was turned towards the observer. This cannot be found from the micrometric measurements, since, although we can obtain from them the amount of the inclination, we cannot determine its sign.

It is also possible that some method of greater delicacy may be discovered, so that the spectroscope may be replaced by a more sensitive instrument, as it has been by the interferential refractometer in measuring the index of refraction of gases.

The semi-axes major of  $\Sigma$  3121, 1768, 2262, and 2055 are not given in the original publications of the orbits. The values inserted in Table V. are those given in the Handbook of Double Stars, by Messrs. Crossley, Gledhill, and Wilson. This work has also proved most useful in various ways in the preparation of this paper. The value of  $a$  given by Dr. Auwers for  $\alpha$  *Canis Majoris* is 2.33. This relates to the ellipse described by the bright star. As the companion is assumed to have a mass  $\frac{1}{2.05}$  times as great as this, the value of  $a$  must be multiplied by 3.05, and therefore  $2.33 \times 3.05 = 7.11$  is the value adopted. It is obvious that for this star the intrinsic brightness of the two components is by no means the same. If the density is the same, the diameter of the companion would be 0.79 that of the primary. The area of its disk would be 0.62, while its light\* is only 0.0001 of that of its primary. The very large relative diameter of  $\gamma$  *Leonis* is remarkable. Its brightness must be about three hundred times that of the Sun, if its density is the same. On the other hand, if no brighter than the Sun, its density would be only one seventh of that of atmospheric air at the standard density and pressure, to give it a sufficient bulk to emit its observed light. If the other binaries have the same density as the Sun, their brightness must vary from 100 in the case of  $\delta$  *Cygni* to 0.06 in the case of  $p$  *Eridani*, the brightness of the Sun being taken as the unit. The semi-axis major and period of 61 *Cygni* are taken from Newcomb and Holden's Astronomy. Although this star is commonly regarded as a binary, the evidence in favor of this view seems to depend upon the large proper motion of both components, and the fact that both appear to be comparatively near the Sun. It is doubt-

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\* Ann. Harv. Coll. Observ., xi. 177.

ful whether the observations yet made are sufficiently exact to prove a connection between the components. To establish this proposition, and also as an example of a convenient means of distinguishing a binary star from one which is optically double, the following investigation is given of the more important observations of 61 *Cygni*. We cannot conclude that a star is binary unless the path described by one of its components appears to be concave with respect to the other. If the motion appears to be rectilinear, it is more probably that due to the proper motion of one of them, or rather to the combined effect of the proper motions of both. On the other hand, if the path is convex, it is extremely probable that there is a real connection between the two, as there is no instance known of a star describing a curved path due to proper motion alone. The motion, if rectilinear, should also be uniform, while, if curved, the motion should be most rapid when nearest the other star. The law that the area described by the radius vector is proportional to the time, cannot be used to distinguish between those motions, since it will apply to both.

Suppose that the measures are transformed to a system of rectangular co-ordinates, having one component as the origin, and the axis of  $X$  nearly parallel to the path of the other component. Except for the accidental errors, the value of  $y$ , if the motion is rectilinear, should be the same for all the observations from the beginning to the end of the series. If the axis of  $X$  is not exactly parallel to the line of motion the values of  $y$  should increase slowly from one end of the series to the other. If they are corrected by an amount which will be proportional to the time, this variation should disappear. If the star is binary, however, the value of  $y$  will vary, in general having its greatest value during the middle of the period, and being smaller at the beginning and end.

The values of  $x$ , if the motion is rectilinear, will vary uniformly with the time, and, if corrected by a constant, plus another constant multiplied by the time, will leave residuals that are very small. If the motion is curved, on the other hand, this condition will not be fulfilled.

A reduction of the observations of 61 *Cygni* is given in Table VI. Of the measurements made during the last half-century only those made by the Struves and by Dembowski have been employed. The position angles are first corrected for precession and reduced to the epoch of 1880 by the formula

$$0^{\circ}.00557 \sin \alpha \sec \delta (t - 1880) = -0^{\circ}.005 (t - 1880).$$

A simple computation shows that the direction of the motion is nearly that of the position angle  $256^\circ$ . We have accordingly,  $y = s \cos (p - 166^\circ)$ , and  $x = s \sin (p - 166^\circ)$ . In the successive

TABLE VI.—PATH OF 61 CYGNI.

No.	Date.	Obs.	Cor. $p$ .	$s$ .	$x$	$y$	$\Delta x$	$\Delta y$
1	1753.8	Bradley.	34.8	19.63	$\rightarrow 12.93$	14.77	$-0.29$	$-0.43$
2	1778.0	Mayer.	50.4	15.24	$-6.59$	13.74	$+0.97$	$-1.46$
3	1781.9	Herschel.	53.3	16.33	$-6.30$	15.07	$+0.44$	$-0.13$
4	1793.6	Lalande.	52.3	14.87	$-5.98$	13.61	$-1.70$	$-1.59$
5	1800.0	Piazzi.	69.8	19.27	$-2.08$	19.16	$+0.86$	$+3.96$
6	1805.0	"	78.1	14.50	$+0.63$	14.49	$+2.42$	$-0.71$
7	1812.3	Bessel.	78.8	16.74	$+0.82$	16.72	$+1.18$	$+1.52$
8	1813.8	Lindenau.	68.8	16.56	$-2.08$	16.43	$-2.04$	$+1.23$
9	1814.5	W. Struve.	68.6	15.20	$-1.96$	15.08	$-2.06$	$-0.12$
10	1820.5	"	83.2	15.11	$+1.89$	14.99	$+0.53$	$-0.21$
11	1822.7	"	85.5	14.93	$+2.46$	14.73	$+0.63$	$-0.47$
12	1828.7	"	89.1	15.31	$+3.47$	14.91	$+0.38$	$-0.29$
13	1831.7	"	90.9	15.63	$+4.02$	15.11	$+0.30$	$-0.09$
14	1832.8	"	91.8	15.79	$+4.30$	15.20	$+0.35$	$0.00$
15	1835.6	"	93.6	15.97	$+4.83$	15.22	$+0.29$	$+0.02$
16	1836.6	"	94.2	16.08	$+5.02$	15.27	$+0.37$	$+0.07$
17	1837.7	"	95.2	15.93	$+5.24$	15.04	$+0.26$	$-0.16$
18	1843.5	O. Struve.	98.8	16.67	$+6.46$	15.44	$+0.26$	$+0.24$
19	1847.5	"	100.7	17.02	$+7.11$	15.46	$+0.07$	$+0.26$
20	1850.3	"	102.3	17.18	$+7.61$	15.40	$+0.01$	$+0.20$
21	1851.8	"	103.5	17.34	$+8.02$	15.38	$+0.08$	$+0.18$
22	1852.7	"	104.4	17.46	$+8.30$	15.36	$+0.17$	$+0.16$
23	1854.2	"	105.1	17.57	$+8.54$	15.35	$+0.10$	$+0.15$
24	1857.2	"	106.4	18.02	$+9.12$	15.55	$+0.05$	$+0.35$
25	1860.8	"	108.6	18.22	$+9.82$	15.35	$-0.01$	$+0.15$
26	1868.5	"	112.4	18.81	$+11.16$	15.14	$-0.28$	$-0.06$
27	1874.7	"	116.1	19.42	$+12.51$	14.85	$-0.24$	$-0.35$
28	1854.7	Dembowski.	105.4	17.29	$+8.49$	15.06	$-0.06$	$-0.14$
29	1855.8	"	106.0	17.34	$+8.67$	15.02	$-0.11$	$-0.18$
30	1856.6	"	106.3	17.45	$+8.80$	15.07	$-0.15$	$-0.13$
31	1857.6	"	107.2	17.73	$+9.19$	15.17	$+0.03$	$-0.08$
32	1858.5	"	107.7	17.73	$+9.32$	15.08	$-0.02$	$-0.12$
33	1862.8	"	109.3	18.36	$+10.08$	15.35	$-0.17$	$+0.15$
34	1863.4	"	109.5	18.37	$+10.14$	15.32	$-0.23$	$+0.12$
35	1864.7	"	110.6	18.63	$+10.44$	15.31	$-0.21$	$+0.11$
36	1865.6	"	110.8	18.57	$+10.60$	15.25	$-0.24$	$-0.05$
37	1867.2	"	111.6	18.72	$+10.90$	15.22	$-0.27$	$+0.02$
38	1868.7	"	112.7	18.83	$+11.25$	15.10	$-0.24$	$-0.10$
39	1869.7	"	113.4	18.96	$+11.52$	15.06	$-0.18$	$-0.14$
40	1870.6	"	113.9	19.16	$+11.77$	15.12	$-0.12$	$-0.08$
41	1871.6	"	114.2	19.23	$+11.89$	15.10	$-0.21$	$-0.10$
42	1872.6	"	114.3	19.33	$+11.98$	15.11	$-0.33$	$-0.09$
43	1873.6	"	114.8	19.44	$+12.18$	15.15	$-0.34$	$-0.05$
44	1874.5	"	115.3	19.50	$+12.35$	15.05	$-0.35$	$-0.15$
45	1875.6	"	115.9	19.58	$+12.56$	15.02	$-0.38$	$-0.18$

columns of Table VI. are given a current number, the date, the name of the observer, the corrected position angle, the distance, and

the values of  $x$  and  $y$ . The value of  $y$  is approximately  $15''.20$ ; that of  $x$ ,  $0''.21$  ( $t - 1814$ ). Residuals are accordingly given in the last two columns by subtracting the values of  $y$  and  $x$  thus obtained from those observed.

The residuals in the last two columns are evidently not due to accidental errors, but whether they are caused by curvature of the path or systematic errors of the observer is less evident. The first nine sets are so discordant, that little dependence can be placed upon them. The values of  $\Delta y$  show a very slight increase, followed by a diminution in the later values.  $\Delta x$  seems to diminish slowly, the later values of the Struves and of Dembowski being somewhat less than the earlier. The curvature is so slight, that it has been thought to indicate an hyperbolic orbit. The observations so far made will however be very nearly satisfied by a large circular orbit seen obliquely, so that the part described during the last century has been that near the end of the minor axis of the apparent ellipse.

If we take the mean of the residuals, we find the values for  $\Delta x$  of  $0''.25$  and for  $\Delta y$  of  $0''.15$ . As these include all kinds of systematic errors, the deviations from a straight line can scarcely be regarded as certain.

## II. VARIABLE STARS OF THE ALGOL TYPE.

Variable stars may be divided into several classes, according to the nature of the fluctuations of their light. First, temporary stars, which appear suddenly, and gradually fade away during the next few months. The most famous star of this class is that observed in 1572, by Tycho Brahe. The new stars in *Corona Borealis* in 1866 and in *Cygnus* in 1876, are recent examples of this class. Second, a large part of the variable stars pass from their maximum to their minimum and back again, in from six months to two years, the period and the brightness at the maximum and minimum being somewhat variable. The change in light is generally very great, amounting to several hundred, or even thousand times. The most striking examples of this class are  $\alpha$  *Ceti* and  $\chi$  *Cygni*. Thirdly, we have the slight changes to which many (or, according to Dr. Gould, most) stars are liable. These changes seem to be irregular in many cases; at least, their law is not yet known. Examples of this class are furnished in  $\alpha$  *Orionis* and  $\alpha$  *Cassiopeiæ*. Fourthly, certain stars continually vary, going through a series of changes in the course of a few days, which appears to be repeated exactly. Two causes seem here to be superimposed, one producing one

maximum and one minimum in each period, the other two maxima and two minima in the same time. As examples,  $\beta$  *Lyræ* and  $\delta$  *Cephei* may be noted. Fifthly, we have a class of stars which during the greater part of the time remain unchanged in brightness, but at regular intervals lose in the course of a few hours a large part of their light, and regain it with equal rapidity. These changes appear to be repeated with the greatest regularity, so that the interval can be computed in some cases within a fraction of a second. *Algol*, or  $\beta$  *Persei*, is the most striking example of this class to which  $\delta$  *Canceri* and  $\delta$  *Libræ* also belong.

Various theories have been advanced to account for these phenomena. Probably different causes act in the case of the different classes. One theory would assume that by a collision, or by the liberation and ignition of a vast amount of hydrogen, the star was suddenly heated to incandescence, and gradually lost its light by cooling. This explanation would apply only to stars of the first class; it is strengthened in the case of the new star in *Cygnus* by the observations with the spectroscope. The spectrum gave at first the lines of incandescent hydrogen which disappeared as the light faded. It has been urged that, to account for the rapid cooling, the star must have been small, perhaps only a few miles in diameter, and consequently not very distant. This view is contradicted by the absence of perceptible parallax. If we consider how quickly a meteorite becomes heated, and again gives up its heat, this argument loses its force. The star may be large and distant, the surface only being heated, and soon losing its heat by radiation and conduction. This explanation appears more probable than that the light is cut off by clouds of smoke or steam, as has been suggested by some astronomers.

Stars constituted like our Sun, but in which the variations in size of the spots would be far greater, might undergo considerable changes in light. While it is difficult to account for the great changes in class two in this way, those in class three may be thus explained. A popular theory for the variation of stars of short period is that it is due to the revolution of the star upon its axis, when the different portions are of unequal brightness. The variation in light of *Iapetus*, the outer satellite of Saturn, is commonly explained in this way. A similar effect would be produced if the star was not spherical, and in revolving exposed a disk of varying area. A great variation could not thus be produced without the revolving body assuming a condition of unstable equilibrium. For the application of these principles to *Iapetus*, see *Annals of Harvard College Observatory*, xi. 264. This theory may ex

plain the variations of stars of the fourth class. Another theory would account for the changes of light by an opaque body or satellite passing between the star and the observer. It will be the object of the following discussion to show how fully this explanation will account for the variations of stars of the fifth class. A modification of this theory would replace the single eclipsing body by a cloud of meteorites. Such a theory will account for almost anything by suitably modifying the distribution of the meteors. If we can show that all the effects may be explained by a single body, or what amounts to the same thing, a spherical cloud of meteors so dense as to be opaque, there seems to be no reason for assuming a cloud of another form. All that can be claimed for any theory is that it explains all the facts. If then the computed variations of light agree with the observations within the limits of errors of observation, that is all that can be asked, and the theory should be accepted as the most probable explanation until some new fact is discovered which it will not explain, or some new theory which agrees equally well with observation and appears to be less improbable. The diminution in light might be caused by the interposition of a body which was self-luminous, instead of dark. We should then have a close double-star, one component of which passed in front of the other. If the orbit was circular, we should have two minima during each revolution, and at these times the star would appear of unequal brightness, unless the intrinsic brightness of the two bodies was the same. When the darker body passed in front of the brighter, the light would be less than when the brighter passed in front of the darker. If the orbit was elliptical there might be only one minimum. In the case of Algol more than half the light is cut off at the minimum; consequently one body must be darker than the other. As no second minimum has ever been observed, it is probable that the eclipsing body is not self-luminous.

We must now show that neither of the other theories named above will explain the variations of Algol and of other stars of the fifth class. The regularity of the variation disposes of the theory of a volcanic eruption, a collision, or a system of sun-spots. These effects also could scarcely be repeated so frequently without exhausting the source of energy from which they were derived. The theory that the variation is due to the revolution of the star appears more probable, and the regularity and shortness of the period add weight to it. On the other hand, it is difficult to account by this theory for the sudden changes in the light. If the light was reduced by a dark portion of the star being turned towards the observer, the minimum should last until, by the



revolution of the star, this part had been turned around so as to disappear on the other side. The short minimum observed could only be caused, according to this theory, by supposing a large dark star with a small bright spot near its polar regions, and that the pole was directed at such an angle, from the observer that a large part of the spot would disappear for a short time during each revolution. Even then we have still the apparently insurmountable difficulty that the bright spot would change its apparent size and the angle at which it emitted its light to the observer, and therefore vary in brightness during the whole period of revolution. No such variation has been established in the light of Algol.

Before showing how far the theory of an eclipsing body will account for the observed phenomena, we must see what knowledge we have of these variations in light.

Only five stars are at present known to belong to the Algol class of variables. These are  $\beta$  *Persei*,  $\delta$  *Canceri*,  $\lambda$  *Tauri*,  $\delta$  *Librae*, and  $\gamma$  *Coronae*. Of these, the first is the only one whose variations are known with sufficient precision to justify a discussion in the present article. The variations of  $\beta$  *Persei*, or Algol, have been carefully studied by three observers, Argelander, Schmidt, and Schönfeld. Argelander's observations extend from 1840 to 1866, and are nearly two thousand in number. He compared Algol from time to time with the adjacent stars of nearly equal brightness, and noted the apparent difference in steps or grades (*Stufen*). Arranging his comparison stars in the order of brightness, and determining the number of grades between each from all his measures, he was then able to denote them all in grades. Thus, suppose at a given time he observed that Algol was slightly, if at all, brighter than star *A*, or that the difference was one grade; again, that it was perceptibly fainter than *B*, or differed from it by two grades; if then he found in his final discussion that  $A = 12.5$  grades and  $B = 14.9$ , the first observation would make Algol 13.5 grades, and the second 12.9. These comparisons are all given in the *Bonn Observations*, vii. 315, but, unfortunately, they have not been reduced, so that at present no use can be made of them. I undertook their reduction, but was informed that this had been done at Bonn. No answer has, however, been received to letters of inquiry on this point.

The observations of Dr. Schmidt extend from 1846 to the present time, and the results up to 1875 are published in the *Astronomische Nachrichten*, lxxxvii. 193. His object was only to determine the time of the minima, and accordingly these only are given, without the comparisons. He also generally used a single comparison star, which



has the advantage of eliminating an error in estimating its brightness, but does not give a good determination of the light curve. Dr. Schönfeld observed Algol, according to the method of Argelander, from 1859 to the present time, and has given the results up to 1870, in the *Sechsendreissigster Jahresbericht des Mannheimer Vereins für Naturkunde*, p. 70. He has not published his comparisons, but has given his resulting light curves, which will be made the basis of the following discussion. We must first reduce his grades to absolute measures, which is done in Table VII. The successive columns give the name of the comparison stars, the light in grades adopted by Schönfeld, the logarithm of the light as measured by Seidel (*Resultate photometrischer Messungen*, München, 1862), the logarithms of the light as measured by Wolff (*Photometrische Beobachtungen an Fixsternen*, Leipzig, 1877), after subtracting 0.232 to eliminate the constant difference between his measures and those of Seidel. The next column gives the difference between the measures of Seidel and Wolff, and shows that on the average they differ only .040, or a tenth of a magnitude. If  $L$  denotes the logarithm of the light, and  $g$  the corresponding number of grades, we may assume  $L = a + gb$ . This is only equivalent to admitting Fechner's law or assuming that Schönfeld's grades correspond to equal ratios of light. A solution by least squares gives  $a = 8.446$  and  $b = 0.025$ , or  $L = 8.446 + 0.025 g$ . The sixth column gives the value of  $L$  computed by this formula for the various values of  $g$  assumed by Schönfeld. The last two columns give the errors of Seidel and Wolff, assuming the estimates of Schönfeld to be exact. The average value of these differences is but little more than a tenth of a magnitude. Apparently,  $\epsilon$  Aurigæ was estimated by Schönfeld about three tenths of a magnitude too bright, and  $\delta$  Persei about two tenths too faint. Omitting these stars the errors would be reduced about one half.

TABLE VII.—COMPARISON STARS FOR  $\beta$  PERSEI.

Name.	Grades.	S	W-0.232	W-0.232 -S	Comp.	S-C	W-C
$\gamma$ Androm.	23.4	9.038	9.021	-.017	9.031	+.007	-.010
$\epsilon$ Aurigæ	17.3	8.697	8.803	+.106	8.878	-.181	-.075
$\beta$ Arietis	16.7	8.897	8.862	-.035	8.864	+.033	-.002
$\epsilon$ Persei	12.8	8.800	8.746	-.054	8.766	+.034	-.020
$\gamma$ Persei	10.9	8.699	8.691	-.008	8.718	-.019	-.027
$\beta$ Trianguli	9.1	8.716	8.716	.000	8.674	+.042	+.042
$\delta$ Persei	7.8	8.741	8.694	-.047	8.641	+.100	+.053
$\alpha$ Trianguli	3.5	8.531	8.588	+.057	8.534	-.003	+.054
$\nu$ Persei	0.9	—	8.435	—	8.468	—	-.033
				±.040		±.052	±.045

Schönfeld has given on page 84 of his memoir a table of his mean results, arranged in seventy-nine groups, seventy-two of them occurring within about four hours and a half of the minimum, and sixty-two within three hours of the minimum. He then drew an empirical curve through these points, and gives their residuals, which vary from  $+0.73$  to  $-0.58$  grades, and have an average value of  $0.17$  grades. Reducing this to logarithms, by multiplying by  $0.025$ , gives  $0.004$ , or only one hundredth of a magnitude. There are thirty-five changes of sign in the residuals, out of a possible seventy-one. There is, therefore, no reason to doubt that the curve represents the observations as nearly as possible.

The light in grades for intervals of every half-hour before and after the minimum is given in Table VIII. The successive columns give the time in hours, the corresponding light in grades before and after the minimum, the difference between these two, their mean, and the corresponding light expressed in logarithms. This is found by subtracting the light in grades from  $20.8$ , which is assumed by Schönfeld as the full brightness of Algol, multiplying the result by  $0.025$  to reduce to logarithms, and taking the arithmetical complement. The number corresponding to this logarithm is given in the last column. It gives the light of Algol, its maximum light being assumed as  $1.000$ .

TABLE VIII.—LIGHT CURVE OF  $\beta$  PERSEI.

Hours.	Dec.	Inc.	D - I	$\frac{D+I}{2}$	Log L	Light.
0.0	5.56	5.56	0.00	5.56	9.619	0.416
0.5	6.26	6.20	$+0.06$	6.23	9.636	0.433
1.0	8.48	7.60	$+0.88$	8.04	9.681	0.490
1.5	12.05	9.81	$+2.24$	10.93	9.753	0.566
2.0	15.28	13.17	$+2.11$	14.22	9.836	0.685
2.5	17.35	15.78	$+1.57$	16.06	9.882	0.762
3.0	18.08	17.71	$+0.97$	18.20	9.935	0.861
3.5	19.59	19.19	$+0.40$	19.39	9.964	0.920
4.0	20.24	20.23	$+0.01$	20.24	9.986	0.968
4.5	20.70	20.75	$-0.05$	20.72	9.998	0.995
4.6	20.8	20.8	0.00	20.80	0.000	1.000

From this table it appears that the law respecting the increase of light is not the same as that of its diminution. At a given interval of time from the minimum, the light is greater when decreasing than when increasing. The mean value will first be considered, and the cause of this difference then discussed.

We shall first assume that the star and satellite present circular

disks, one uniformly bright, the other dark, and that the form of orbit is circular. Three cases may occur, corresponding to a total, an annular, and a partial eclipse of the star. In the first case, all the light would be cut off for a longer or shorter time; in the second, the minimum light would be maintained during the transit of the satellite across the face of the star; and in the third case the light would diminish until the minimum was attained and then immediately begin to increase. Algol appears to belong to the last of the classes. We must next determine the relative diameters of the satellite and star. A minimum diameter of the satellite may be computed from the minimum light. To reduce the light to 0.416, or to cut off 0.584 of the light, the diameter of the satellite must be at least  $\sqrt{0.584} = 0.764$  times that of the star. In this case it would just pass completely on to the disk before it began to pass off. No maximum can be determined in this way, so that the diameter is only limited between 0.764 and infinity. A change in diameter will, however, produce a change in the law of variation of the light. We may deduce the diameter from the values agreeing most nearly with observation. We must now determine the amount of light remaining when the star is partially eclipsed by a satellite of radius  $r$ . The radius of the star is taken as the unit. The area of the segment of a circle of radius unity whose versed sine is  $z$ , is equal to  $\text{versin}^{-1} z - (1 - z) \sqrt{2z - z^2}$ . A table is given in the eighth edition of the *Encyclopædia Britannica*, xiv. 525, Art. *Mensuration*, which gives this quantity for values of  $z$  varying by hundreds from 0.00 to 1.00. The portion of the disk cut off will always be composed of two segments having the radii 1 and  $r$ , and having a common chord which may be computed when we know the distance of the centres. The area of each may be taken from the table, multiplied by the square of the radius of its circle, and the two areas added. This will give the required diminution in light.

If now we assume  $r$  the radius of the satellite, several of the elements may be computed.

The period of revolution of the satellite is given with much precision from the observations of the minima. It appears to undergo slight changes, but may be assumed for the present time to equal 2 days 20 hours 48.9 minutes. Calling  $w$  the longitude of the satellite in its orbit reckoned from its minimum, the mean change in  $w$  per hour will equal  $5^{\circ}.023$ . Since the beginning and ending of the obscuration precede and follow the minimum by  $4^h 35^m$ , the corresponding values of  $w$  will be  $337^{\circ}.0$  and  $23^{\circ}.0$ . At these points the centre of the satellite will be at a distance  $(1 + r)$  from the centre

of the star, or the disks will touch each other. They correspond to the first and last contacts of an eclipse. The orbit is projected into an ellipse whose major axis,  $a$ , equals the true distance of the centres, and whose minor axis,  $b$ , equals the distance at the time of greatest obscuration. When  $r = 0.746$ ,  $b = 1 - 0.746 = 0.254$ . For other values of  $r$ ,  $b$  must be determined from a computation of the area eclipsed, by successive approximations, until such a value is found as will reduce the light to 0.416. If  $x$  and  $y$  are the co-ordinates of the point in the orbit reached by the satellite at the time of first contact, by the properties of the ellipse  $x = a \sin w$ , and  $y = b \cos w$ . The square of the distance of the centres, or  $D^2$ , may be written

$$D^2 = (1 + r)^2 = (x^2 + y^2) = a^2 \sin^2 w + b^2 \cos^2 w \\ = a^2 - (a^2 - b^2) \cos^2 w.$$

Since  $w = 23^\circ.0$ ,

$$(1 + r)^2 = 0.153 a^2 + 0.847 b^2.$$

Substituting the proper values of  $r$  and  $b$ ,  $a$  may be deduced. The cosine of the inclination,  $i$ , of the orbit will equal  $\frac{b}{a}$ . The three lines of Table IX. give the values of  $a$ ,  $b$ , and  $i$  computed by these formulas for the minimum value of  $r = 0.764$ , for  $r = 1.000$ , and for  $r = 2.000$ . There is no maximum value of  $r$ , which may be indefinitely large. Let  $R$  be any large value of  $r$ , and let  $a = R + A$ ,  $b = R + B$ , and  $D = R + d$ ; substituting these values in the formula,  $D^2 = a^2 \sin^2 w + b^2 \cos^2 w$ , the terms containing  $R^2$  cancel each other, and we have  $2 R d = 2 R A \sin^2 w + 2 R B \cos^2 w$ , omitting the terms not containing  $R$ , since when  $R$  is very large they may be neglected. Dividing both sides by  $2 R$  gives  $d = A \sin^2 w + B \cos^2 w$ . When  $w = 23^\circ$ ,  $d$  must equal 1, and when  $w = 0^\circ$ ,  $B$  will equal  $-0.132$ , since the arc of the large circle becomes sensibly a straight line, and the segment whose versed sine is  $1.000 - 0.132$  has an area of 0.416, or the minimum area of the uneclipsed portion. From these values, we may deduce  $A = 7.300$ . The two axes, therefore, become  $R - 0.132$  and  $R + 7.300$ . The inclination in this case continually diminishes as  $R$  increases, and would equal zero if  $R$  became infinite.

The residuals which will be deduced below at first led to the belief that the phenomenon might be that of an annular eclipse. This case has therefore been included to show the change effected in the variation of the light, although the residuals are not materially reduced. If the eclipse is annular, the value of  $r$  must be 0.764.

The value of  $b$  cannot be determined directly, but must be deduced from the times of internal and external contact. The interval between the internal contacts is assumed to be 24 minutes, or that during which the satellite moves through  $2^\circ$  of longitude. In the equation  $D^2 = a^2 \sin^2 w + b^2 \cos^2 w$ , we have for  $w = 1^\circ$ ,

$$D = (1 - r) = 0.236,$$

and as before for  $w = 23^\circ$ ,

$$D = 1 + r = 1.764.$$

From these conditions the values of  $a$  and  $b$  given in the last column of Table IX. are deduced.

TABLE IX.—ELEMENTS OF ORBITS.

Elements.	$r = 0.764$	$r = 1.000$	$r = 2.000$	$r = R$	Ann.
Minor semi-axis, $b$	0.236	0.666	1.783	$R - 0.132$	0.223
Major semi-axis, $a$	4.480	4.872	6.427	$R + 7.300$	4.482
Inclination, $i$	$87^\circ.0$	$82^\circ.1$	$73^\circ.9$	Small.	$87^\circ.1$

We must next compute the amount of obscuration at the end of each half-hour, for the various values of  $r$ . The distance between the centres is first computed by the equation  $D^2 = a^2 - (a^2 - b^2) \cos^2 w$ , substituting successively,  $w = 2^\circ.5, 5^\circ.0, 7^\circ.5, 10^\circ.0, 12^\circ.6, 15^\circ.1, 17^\circ.6$ , and  $20^\circ.1$ . The first part of Table X. gives the values of  $D$  corresponding to those assigned to  $r$  at the head of each column. The triangles formed by the centres of the two bodies and one end of the segment now become known, since their three sides equal 1,  $r$ , and  $D$ . Calling the angle at the centre of the luminous body  $\alpha$ , we have  $r^2 = 1^2 + D^2 - 2 D \cos \alpha$ . From this we deduce  $\cos \alpha$  and  $\text{versin } \alpha$ , or the height of the segment bounded by the circle having a radius unity. The height of the other segment will equal  $R - D + \cos \alpha$ , from which the areas of the segment, and consequently of the uneclipsed portion, may be deduced. This area is given in the second portion of the table. For comparison the observed light is repeated in the last column from the last column of Table VIII. The residuals, or the observed values minus those computed with each value of  $r$ , are given in the third part of Table X. The residuals are all zero when the time equals 0.0 or 4.6, and are therefore omitted. The average residuals are given in the last line.

TABLE X.—DISTANCES OF CENTRES.

Hours.	0.764	1.00	2.00	R—D	0.764
0.0	0.236	0.666	1.783	—0.132	0.223
0.5	0.307	0.700	1.806	—0.116	0.298
1.0	0.463	0.794	1.865	—0.072	0.457
1.5	0.629	0.917	1.957	—0.005	0.625
2.0	0.811	1.072	2.081	+0.092	0.807
2.5	0.988	1.233	2.223	+0.211	0.986
3.0	1.191	1.425	2.404	+0.375	1.190
3.5	1.373	1.606	2.583	+0.548	1.372
4.0	1.556	1.789	2.773	+0.748	1.555
4.6	1.764	2.000	3.000	+1.000	1.764

LIGHT OF UNECLIPSED PORTION.

Hours.	0.764	1.00	2.00	R	0.764	Obs.
0.0	0.416	0.416	0.416	0.416	0.416	0.416
0.5	0.434	0.436	0.432	0.427	0.430	0.433
1.0	0.500	0.491	0.469	0.454	0.497	0.480
1.5	0.579	0.562	0.527	0.497	0.578	0.566
2.0	0.668	0.648	0.603	0.559	0.667	0.685
2.5	0.751	0.731	0.686	0.633	0.750	0.762
3.0	0.838	0.822	0.785	0.733	0.838	0.861
3.5	0.907	0.898	0.874	0.831	0.907	0.920
4.0	0.968	0.959	0.949	0.927	0.968	0.968
4.6	1.000	1.000	1.000	1.000	1.000	1.000

RESIDUALS.

Hours.	0.764	1.00	2.00	R	0.764
0.5	— .001	— .003	+ .001	+ .006	+ .003
1.0	— .020	— .011	+ .011	+ .026	— .017
1.5	— .013	+ .004	+ .039	+ .069	— .012
2.0	+ .017	+ .037	+ .082	+ .126	+ .018
2.5	+ .011	+ .031	+ .076	+ .129	+ .012
3.0	+ .023	+ .039	+ .076	+ .128	+ .023
3.5	+ .013	+ .022	+ .046	+ .089	+ .013
4.0	.000	+ .009	+ .019	+ .041	.000
	± .012	± .020	± .044	± .077	± .012

The residuals are all expressed in terms of the full light of the star. They therefore represent a larger error expressed in logarithms, or stellar magnitudes, when the star is faint than when it is bright. If reduced to logarithms their mean values become .008, .012, .027, .049, .008. Dividing these quantities by 0.4 to reduce them to magnitudes,

we see that while a large value of  $r$  would give an average residual of over one tenth of a magnitude, the value of  $r = 0.764$  would make this quantity less than two hundredths of a magnitude. In all of them, however, there is a distinct systematic variation, the computed light being too small when  $t$  is large, and sometimes becoming too large when  $t$  is small. It appeared that this error might be reduced by assuming that the eclipse was annular, or that the light retained its minimum value for a short time. The corresponding residuals are given in the last column. They reduce the positive residuals when the star is faint, but do not sensibly affect the others, although the time between the internal contacts is assumed to be twenty-four minutes. The observations scarcely admit so great an interval, and certainly would not justify its increase. As the average residual is not diminished by the assumption of an annular eclipse, and as the observations do not indicate that the light remains constant during the minimum, we cannot do better than to assume the value of  $r = 0.764$ , and adopt the values of the second column of the table.

Several explanations may be offered of the small systematic error that remains. The most plausible seems to be that derived from the residuals given in the last column of Table VII. They show that, from a comparison of the estimated grades of Schönfeld with the measures of Wolff, that Schönfeld estimated the light too faint when the star was faint, and too bright when the star was bright. In other words, that a grade did not have the same values when expressed in logarithms for a faint as for a bright star. Assuming the photometric measures of Wolff to be free from systematic error, we should therefore increase the estimates of Schönfeld when the star was faint, and diminish them when it was bright, without affecting the actual maximum and minimum values. Such a correction would make the systematic error noted above disappear, or even give it an opposite sign. This view receives a slight confirmation from the measures of Seidel, but the accidental discrepancies far exceed this small systematic error. We may therefore conclude that the computed light agrees with observation as closely as the brightness of the fundamental stars is at present known, and there is no evidence of a real systematic difference between the two.

Another explanation of the residuals in Table X. has suggested itself. The presence of lines in stellar spectra leads to the belief that the stars, like our Sun, are surrounded by an absorbing atmosphere. They also, therefore, probably resemble it in presenting a disk brighter in the centre than at the edges, owing to the greater thickness of the



atmosphere and consequent greater absorption at the edges. The effect of such an absorption is best determined by the consideration that if, owing to absorption, the average light of the eclipsed portion is less than that of the whole disk, the effect of the atmosphere will be to diminish the proportion of the light cut off; in the opposite case, it will increase it. Now when a small portion only of the star is eclipsed, evidently the average light of this portion, since it lies near the edge, must be less than that of the whole. The atmosphere, although then diminishing the light of the remaining portion, will not reduce it as much as it does that of the entire disk; the relative light will therefore be increased. On the other hand, when a large part of the eclipsed portion is from the central and brightest portion the opposite effect will be produced. We should therefore expect, when  $t$  is large, that the computed light should be increased. When  $t$  is small, it may be diminished. In the case of the Sun the effect is so slight, except close to the borders, that the previous explanation seems more probable.

We return now to the consideration of differences in the rate of diminution and increase of the light. The observations ought to give this quantity with much accuracy. An error in estimating the light of the standard stars will not sensibly affect it, since the same stars are used in measuring the increase and diminution. The effect of atmospheric absorption is reduced, since some of the comparison stars are always above and others below the variable, and besides, although, when observed before passing the meridian, the star is brighter when increasing than when diminishing, yet the opposite effect is produced when the star is west of the meridian. Nevertheless this difference is doubted by many astronomers, and if it exists it is evident that an important correction should be applied to the observed minima of Algol. If the curve found by Schönfeld is correct, an error of ten minutes in the time of the minimum might be caused by comparing with a star like  $\epsilon$  *Persei*, having a brightness of about twelve grades, and taking the mean of the times when the two stars appeared equal.

Three explanations may be offered for this phenomena. First, that the satellite is not spherical, but egg-shaped, and that the large end is turned forwards; or that the satellite is of unequal density, and that the heaviest portion is forward. In this case the centre of gravity of the disk would follow that of the satellite, or for a given distance of the centres the interposed area would be greater when the satellite was passing off, than when coming on. So great a deviation from the spherical shape would be needed to produce the observed difference



that this theory does not seem very probable. We should also, in this case, assume that the time of revolution was exactly equal to that of rotation of the satellite. A second explanation would assume that one portion of the disk of Algol was darker than the rest, so that when the satellite entered the disk it would cut off the dark portion, or affect the light less than when passing off and obscuring the brighter parts. In this case we must assume that Algol does not rotate, or it would show a variation independent of the eclipse by its satellite. Its axis of rotation might be parallel to the path of the satellite and the variations in light on its surface be distributed in zones, but such a theory seems improbable. The third explanation is that the orbit of the satellite is elliptical, and that the difference is due to the varying velocity of the satellite.

An analytical solution of this problem may be found by reducing the observed light to distances of centres, either by interpolation from the values computed above, or by successive approximations. The case then becomes that of a binary star, in which we have given the period and a number of distances, but no position angles. It is of course impossible to deduce the position angles of the peri-astron or other point of the orbit, but its other dimensions may be determined. The solution of this problem will be undertaken at another time should the accumulation of observations of Algol and other similar stars render it desirable. For the present, it will be sufficient to obtain an approximate solution. The nature of the variation is not so simple as would appear at first sight; since the observed time of increase equals that of diminution, we must assume that the apparent motion, when compared with that in a circular orbit, is less at the beginning and end, and greater in the middle of its path. The satellite must therefore either pass its peri-astron during the eclipse, or it must be approaching this point, so that the increased obliquity of its path to the line of sight will produce the apparent diminution in its motion. An ellipse was constructed, having an eccentricity of 0.5 and divided into thirty-two parts, corresponding to the position of the satellite at the end of each thirty-second of its time of revolution. The eccentric anomaly was derived from the mean anomaly by the tables of Dr. Doberck, *Astronomische Nachrichten*, cxii. 275.

As the time of eclipse is very nearly one eighth of that of revolution, four of these divisions correspond to the passage of the satellite over the star. Laying this ellipse on a sheet of rectangular paper and turning it around its focus, the effect of a change in the position of the peri-astron could be determined. The problem is greatly sim-

plified by the fact that the apparent path of the satellite during the eclipse is nearly rectilinear. It was found that, if the longitude of the line of nodes was made equal to  $17^\circ$ , the periods of ingress and egress would be nearly equal. The peri-astron then happens to coincide with the point of egress. The variation in light due to this orbit is compared with observation in Table XI. The successive columns give the time, the observed light in grades, the logarithm of this light, and its value compared with the full light of the star. The next column gives the light already found in the second column of the second part of Table X., and which may be called *A*. The next column gives the variation in light for the elliptical orbit assumed above, which will be denoted as *B*. The second part of the table gives the residuals found by subtracting these values of the light from those observed. The last columns give the residuals found by subtracting the logarithms of these quantities. Although the residuals even of *A* are not very large, they are systematic, being positive when the light diminishes, and negative when it increases. The residuals *B* are much smaller than those of *A* during ingress, but they are larger during egress. In other words, while the systematic error of ingress has been nearly eliminated, a nearly equal error has been introduced during egress. Accordingly the average residual is not diminished. We have so far adopted the times of first and last contact given by Schönfeld. An inspection of the table from which he derived his curve shows that the weight he assigns to his observations when more than three hours from the minimum is small, and that consequently the times of contact must be somewhat uncertain. The exact time of minimum must also be uncertain, although to a less degree than that of the two points just mentioned. An approximate solution by least squares was therefore made, with the times of contact and of minimum as unknown quantities. One half weight was given to the equations of condition formed from the observed terms of contact. From this a correction to the observed minimum was found of 5 minutes, or the true minimum appears to occur nearly one tenth of an hour later than that given by the curve. The time of first contact should also be diminished by about 2 minutes, and the time of last contact increased by about 13 minutes. The columns *C* give the values of the light and of the residuals corresponding to this orbit. The third place of decimals is not always exact, as this would have involved a great increase in the labor of computation and the accuracy attained appears to be all that is at present justified by the observations.

The residuals thus obtained are quite satisfactory as regards their

magnitudes and the number of changes of sign, but the orbit is open to a criticism of a wholly different kind. Its semi-axis major is only 3.55, and as the eccentricity is 0.500, the distance of the centres at peri-astron is 1.775. Now as the radius of the star is 1.000 and of the satellite .764, it is evident that, although they would not actually

TABLE XL.—COMPARISON OF ORBITS.

Hours.	Grades.	Log L	L	A	B	C	D
4.6	20.8	1.000	1.000	1.000	0.999	1.000	1.000
4.0	20.24	0.986	0.968	0.968	0.982	0.986	0.987
3.5	19.59	0.970	0.933	0.907	0.945	0.949	0.937
3.0	18.68	0.947	0.885	0.838	0.883	0.890	0.866
2.5	17.35	0.914	0.820	0.751	0.809	0.815	0.788
2.0	15.28	0.862	0.728	0.668	0.714	0.725	0.697
1.5	12.05	0.781	0.604	0.579	0.613	0.626	0.601
1.0	8.48	0.692	0.492	0.500	0.517	0.534	0.518
0.5	6.26	0.636	0.432	0.434	0.440	0.450	0.446
0.0	5.56	0.619	0.416	0.416	0.416	0.416	0.416
0.5	6.20	0.635	0.432	0.434	0.440	0.429	0.426
1.0	7.60	0.670	0.468	0.500	0.515	0.494	0.486
1.5	9.81	0.725	0.531	0.579	0.603	0.576	0.570
2.0	13.17	0.809	0.614	0.668	0.695	0.665	0.660
2.5	15.78	0.874	0.748	0.751	0.785	0.754	0.753
3.0	17.71	0.923	0.838	0.838	0.858	0.830	0.839
3.5	19.19	0.960	0.912	0.907	0.926	0.899	0.909
4.0	20.23	0.986	0.968	0.968	0.975	0.953	0.970
4.6	20.8	1.000	1.000	1.000	1.000	0.995	1.000

Hours.	A	B	C	D	A	B	C	D
4.6	.000	-.001	.000	.000	.000	.000	.000	.000
4.0	.000	-.014	-.018	-.019	.000	-.006	-.008	-.008
3.5	+.026	-.012	-.016	-.004	+.012	-.005	-.007	-.002
3.0	+.047	+.002	-.005	+.019	+.024	+.001	-.002	+.009
2.5	+.069	+.011	+.005	+.032	+.038	+.006	+.003	+.018
2.0	+.060	+.014	+.003	+.031	+.037	+.008	+.002	+.019
1.5	+.025	-.009	-.022	+.003	-.018	-.007	-.016	+.002
1.0	-.008	-.025	-.042	-.026	-.007	-.022	-.036	-.022
0.5	-.002	-.008	-.018	-.014	-.002	-.008	-.017	-.013
0.0	.000	.000	.000	.000	.000	.000	.000	.000
0.5	-.002	-.008	+.003	+.006	-.003	-.009	+.003	+.006
1.0	-.032	-.047	-.026	-.018	-.029	-.042	-.024	-.017
1.5	-.048	-.072	-.045	-.039	-.038	-.055	-.035	-.031
2.0	-.024	-.051	-.021	-.016	-.016	-.033	-.014	-.011
2.5	-.003	-.037	-.006	-.005	-.002	-.021	-.003	-.003
3.0	.000	-.020	+.008	-.001	.000	-.011	+.004	-.001
3.5	+.005	-.014	+.013	+.003	+.002	-.007	+.006	+.001
4.0	.000	-.007	+.015	-.002	.000	-.003	+.007	-.001
4.6	.000	.000	-.005	.000	.000	.000	-.002	.000
	±.018	±.019	±.014	±.012	±.012	±.013	±.010	±.009

touch, yet they would come so near that the least disturbance would at once produce a catastrophe. This, therefore, gives the limiting value to the eccentricity. A computation with a smaller eccentricity gave less satisfactory residuals. The question now arises, will it not be possible to satisfy the observations by returning to the circular elements, since we have permitted a change in the times of contact and of minimum. Columns *D* give the residuals for a circular orbit with a diminution of 0.1 hour in the time of minimum, and assuming that the periods of ingress and egress are each equal to 4.45 hours instead of 4.6 hours. In other words the ingress occurs about fourteen minutes later, and the egress two minutes earlier, than was assumed by Schönfeld.

The errors which remain, even in the last orbit, are not wholly accidental; but their values are so small, and the changes of sign so frequent, that it is not safe to base important conclusions upon them. Their average value is only .012, or expressed in logarithms .009, and in magnitudes .02. Accordingly, we may compute the variation in the light of Algol, which shall not differ from observation on an average more than a fiftieth of a magnitude. If then this is not the true cause of the variation of the light, it at least satisfies it well within the errors of observation. The orbit *D* may therefore be adopted as representing the law of variation as well as it is at present known.

The stellar magnitude of Algol is about 2.0, so that by Table II., if its brightness equals that of the Sun, its diameter will equal  $0''.006$ . The diameter of the orbit of the satellite will be about  $0''.028$ . The motion of the bright star, if its density is the same as that of its satellite, will equal  $0''.009$ , since its mass in this case will be to that of its satellite as 1.000 is to 0.446. It would therefore be useless to attempt to observe the motion micrometrically. For the same reason, there seems to be no means by which we can determine the position angle of the satellite, or the direction of the axes of the ellipse into which the orbit is projected. Even if future observations should render a larger value of the radius probable, the motion would be scarcely perceptible micrometrically. If  $r = 2.000$ , the diameter of the orbit becomes  $0''.08$  and the motion of Algol about  $0''.07$ . It would be difficult to measure so small a quantity, although, as it is traversed in less than a day and a half, many sources of systematic error would be eliminated.

Below are given, in successive columns, the corresponding values of several elements of the orbits *A*, *B*, *C*, and *D*. The diameter of Algol is assumed to be  $0''.006$ . The times are given in minutes from the

minimum adopted by Schönfeld. A negative sign denotes that the time precedes the minimum; a positive, that it follows it.

Elements.	A.	B.	C.	D.
Eccentricity . . . . .	0.00	0.50	0.50	0.00
Semi-axis major . . . . .	0".0134	0".0109	0".0106	0".0138
Inclination . . . . .	87°.0	84°.3	84°.2	87°.1
Longitude of nodes . . . . .	—	17°	17°	—
Time of first contact . . . . .	—276	—279	—278	—261
“ minimum . . . . .	0	—1	+5	+6
“ last contact . . . . .	+276	+273	+289	+273

The elliptical orbits *B* and *C* are much smaller than the others. Since the eclipse takes place near the peri-astron, the angular motion is so great that the radius vector must be reduced to maintain the same duration of eclipse.

To give a more tangible idea of the dimensions of this system a projection is given of the orbit denoted by *D* in its own plane in Fig. 1,



Fig. 1.

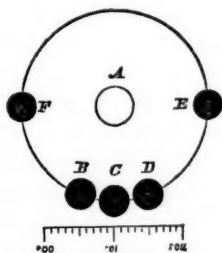


Fig. 2.

and as seen from the Earth in Fig. 2. In both projections *A* denotes the primary, *B* the satellite at first contact, *C* when half across the disk, *D* at the last contact, and *E* and *F* at its elongations. The scale is one hundredth of a second to a centimeter. Accordingly, if Fig. 2 is removed to a distance of 206 kilometers, or about 120 miles, it would appear of the same size as Algol when seen from the Earth.

The application of the spectroscope to this binary star offers a most interesting field for work. Assuming the same data as before, we find the circumference of the orbit equals  $2\pi \times 0".0138 = 0".087$ ; or

multiplying by 0.446 and dividing by 1.446 will give a motion of Algol of  $0''.027$  in each revolution. This corresponds to  $3''.43$  annually. If the parallax of Algol is  $0''.1$ , this would correspond to a velocity of about 160 kilometers (100 miles) per second. Substituting the values in the equation on page 9,  $v = 13\ l$ , we have  $l = 2.6$ , or the  $F$  line would be deviated through an interval equal to nearly half the space between the  $D$  lines. Moreover, as this quantity would be alternately positive and negative every thirty-five hours, the systematic errors which are so troublesome in such measures could be eliminated, and the quantity to be observed would be doubled. If the parallax of the star is more than  $0''.1$  the motion would be less, but on the other hand the parallax would then become a suitable object for micrometric measurement. If the parallax is much less than  $0''.1$  the motion would be so large that its variations might be determined with some accuracy, and the form of the orbit computed from the varying velocity along the line of sight. These measures would also determine the dimensions of the orbit, and if we assume the value of the brightness,  $l$ , they would give the distance and parallax of the star. The spectrum of Algol has already been examined without the detection in it of any peculiarity. The time selected for observation would be more likely to be near its minimum, to detect any changes in the spectrum accompanying its variation in light. But this is the very time when the motion along the line of sight is zero, which may be the reason why this phenomenon has as yet escaped detection.

Two objections have been offered to the theory that the variation in light was due to the interposition of a non-luminous satellite. First, the large size of the satellite; and, secondly, the rapidity of its motion. It has been said that, according to the prevalent theories regarding the formation of the stars, so large a body could not well have lost all its heat while the luminous star is still so bright. This argument would have some force, if we were sure of the true origin of the stars, and also if we knew that both bodies are of the same age. They may, however, have had a wholly independent origin, and have come together through their proper motion, under the influence of a resisting medium or other disturbing force.

The objection to the rapidity of motion cannot be defended in that form. By the law of gravitation we can compute what should be the velocity with a given density, and the only proper criticism would be that to produce the observed velocity an improbable density would be required. To determine this density we may use the formula of

page 6 for the equivalent diameter of the system, using as a unit the radius of the star. We thus find,  $b = 0.00933 a P^{-\frac{1}{3}} = 0.00933 \times 4.60 (0.00785)^{-\frac{1}{3}} = 1.087$ . Accordingly, a body having the density of the Sun, and a diameter but little more than half that of Algol, would give the observed time of revolution to the satellite. If, therefore, the velocity is remarkable, it is remarkable that it is not greater. If the satellite of Algol has a diameter of 0.764, and its density equals that of the primary, its relative mass will be 0.446. The two bodies combined would form a sphere having a radius of 1.130 and a diameter of 2.260. This is 2.08 times that of the equivalent diameter, and shows that the average density can be only 0.11 of that of the Sun, or about one seventh of that of water.

It may be noted that the density affords a means of distinguishing between a satellite and a spherical cloud of meteors. If the individual meteors were very minute, they might completely cut off the light, and yet bear a very small ratio in volume to the space between them. Accordingly, if the density of the eclipsing body could be shown to be very small, we might infer that it was composed of meteorites. In this case the motion of Algol would be insensible, as seen in the spectroscope.

The observed times of minima of Algol seem to show that its period has undergone a diminution during the last century. Such a change is easily explained on the theory of a secondary satellite. The disturbance caused by a third body, or by a resisting medium, might very sensibly vary the period from year to year. The law of this change is not yet known, but its nature is shown in Table XII. The minima are distinguished by successive numbers,  $E$ , that occurring on Jan. 1, 1800, being designated as 0. Those preceding 9000 have been arranged in groups of 500 each. Since 1870 the observations of each year are grouped together. The successive columns of the table give a current number, the mean of the numbers of the minima, the corresponding year and tenth and the number of minima included in the group. In the last nine groups, which relate to a single year, the minimum corresponding to opposition is used, instead of the mean of those observed.

The first eleven sets were observed by various astronomers; sets 12 to 18 were made by Argelander; sets 19 to 21 by Schönfeld; and sets 22 to 30, by Schönfeld and Schmidt. Sets 18 and 19 relate to the same period of 500 revolutions from 7500 to 8000. The fifth column is found by subtracting from the observed time that given by the formula of Schönfeld on page 94 of his memoir, —



Ep.  $E = 1867$ , Jan. 0 <sup>d</sup> 11 <sup>h</sup> 1.2 <sup>m</sup> M. Z. Paris + 2 <sup>d</sup> 20 <sup>h</sup> 48.9 <sup>m</sup> ( $E - 8534$ ).

For the earlier observations the reduction given by Argelander (*Bonn Observations*, p. 347) are used, after reducing them to the above formula by subtracting  $355^m - 0.0749 E$ . The sixth column gives the ordinates of a smooth curve without points of inflection drawn through the points whose abscissas and ordinates are respectively given in the third and fifth columns. The last column gives the difference between the fifth and sixth columns.

TABLE XII.—MINIMA OF ALGOL.

No.	Mean Epoch.	Date.	No. Min.	Obs.	Curve.	O. — C.
1	— 2101	1783.5	27	— 510	— 507	— 3
2	— 1860	1785.4	17	— 488	— 480	+ 1
3	— 1308	1789.8	17	— 450	— 446	— 4
4	— 706	1794.5	6	— 400	— 401	+ 1
5	— 250	1798.0	10	— 368	— 367	— 1
6	+ 214	1801.7	2	— 308	— 332	+ 24
7	+ 734	1805.7	2	— 280	— 293	+ 13
8	+ 1831	1814.4	2	— 211	— 210	— 1
9	+ 2282	1817.9	6	— 180	— 177	— 3
10	+ 2574	1820.2	5	— 155	— 155	0
11	+ 3212	1825.2	3	— 114	— 108	— 6
12	+ 4081	1832.0	2	— 44	— 46	+ 2
13	+ 5259	1841.3	16	+ 25	+ 24	+ 1
14	+ 5741	1845.1	4	+ 37	+ 25	+ 12
15	+ 6154	1848.4	6	+ 24	+ 24	0
16	+ 6838	1853.7	16	+ 21	+ 20	+ 1
17	+ 7308	1857.4	17	+ 10	+ 15	— 5
18	+ 7688	1860.4	4	— 1	+ 11	— 12
19	+ 7799	1861.3	5	— 5	+ 9	— 14
20	+ 8374	1865.9	12	+ 2	+ 2	0
21	+ 8791	1869.0	15	— 1	— 5	+ 4
22	+ 9026	1870.9	13	+ 1	— 8	+ 9
23	+ 9153	1871.9	12	— 4	— 10	+ 6
24	+ 9281	1872.9	19	— 7	— 12	+ 5
25	+ 9408	1873.9	16	— 1	— 14	+ 13
26	+ 9535	1874.9	4	— 8	— 17	+ 9
27	+ 9662	1875.9	9	— 7	— 20	+ 13
28	+ 9789	1876.9	13	— 22	— 23	+ 1
29	+ 9916	1877.9	9	— 46	— 26	— 20
30	+ 10043	1878.9	4	— 29	— 29	0

The numbers in the last column nearly equal the accidental errors of observation. There is a slight grouping of negative signs about 1860, and of positive signs soon after 1870. This could not be avoided without giving to the curve a point of inflection. The average value of these residuals is about six minutes, which shows the accordance to be expected from any assumed formula.



Adopting the curve described above as representing the true variation, its ordinates for every ten years have been read off, and are given in the third column of Table XIII. The direction of its tangent has also been determined, and the seconds of the resulting period is entered in the fourth column. To this is to be added  $2^d\ 20^h\ 48^m$ . The second column gives approximately the corresponding value of  $E$ .

TABLE XIII. — VARIATION OF PERIOD.

Year.	$E$ .	Curve.	Period.
		m.	s.
1780	— 2545	— 541	58.6
1790	— 1273	— 444	58.6
1800	0	— 348	58.5
1810	+ 1273	— 252	58.5
1820	+ 2545	— 157	58.4
1830	+ 3818	— 64	58.3
1840	+ 5090	+ 16	58.6
1850	+ 6363	+ 24	58.7
1860	+ 7635	+ 11	58.3
1870	+ 8908	+ 7	58.0
1880	+ 10180	+ 31	52.7

An inspection of the curve of variation of the times of minimum shows that a curious change took place between 1830 and 1850. Before then, the period given by Wurm of  $2^d\ 20^h\ 48^m\ 58.5^s$  represents the observations well; after 1850, the formula of Schönfeld appears to be more nearly correct. There seems, during this interval, to have been a change of four or five seconds in the period, and that besides this there has been a small but gradually increasing diminution in the period throughout the century.

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## II.

APPENDIX TO PAPER ON THE MECHANICAL EQUIVALENT OF HEAT, CONTAINING THE COMPARISON WITH DR. JOULE'S THERMOMETER.

By H. A. ROWLAND.

Presented, March, 1880.

In the body of this paper I have given an estimate of the departure of Dr. Joule's thermometer from the air thermometer, based on the comparison of thermometers of similar glass. But as it seemed important that the classical determinations of this physicist should be reduced to some exact standard, I took to England with me last summer one of my standards, — Baudin, No. 6166, — and sent it to Dr. Joule with a statement of the circumstances. He very kindly consented to make the comparison, and I now have the results before me. These confirm the estimate that I had previously made, and cause our values for the equivalent to agree with great accuracy. The following is the table of the comparison.

Readings.		Temperatures.		
Baudin, No. 6166.	Joule.	By perfect Air Thermometer according to No. 6166.	By Joule's Thermometer.	Difference.
21.88	22.62	0	0	0
41.930	59.410	1.590	1.578	— .012
48.782	72.200	2.126	2.127	+ .001
53.705	81.340	2.511	2.519	.008
58.916	90.877	2.918	2.928	.010
64.914	101.777	3.382	3.396	.014
73.374	117.291	4.039	4.061	.022
80.176	129.990	4.567	4.606	.039
85.268	139.255	4.961	5.003	.042
90.564	148.834	5.370	5.414	.044
94.243	155.460	5.654	5.698	.044
99.168	164.400	6.036	6.082	.046

Readings.		Temperatures.		
Baudin, No. 6166.	Joule.	By perfect Air Thermometer according to No. 6166.	By Joule's Thermometer.	Difference.
104.030	173.140	6.413	6.457	.044
108.863	182.040	6.789	6.839	.050
113.706	190.885	7.165	7.218	.053
114.000	191.382	7.188	7.239	.051
*121.507	*219.497	*7.772	*8.445	...
135.858	231.115	8.890	8.944	.054
140.467	239.939	9.249	9.309	.060
143.405	245.006	9.479	9.540	.061
146.445	250.566	9.717	9.778	.061
152.360	261.481	10.180	10.246	.066
158.770	273.239	10.681	10.751	.070
164.635	283.957	11.138	11.211	.073
170.485	294.739	11.595	11.670	.075
175.436	303.682	11.979	12.057	.078
182.795	316.968	12.550	12.627	.077
188.705	327.746	13.008	13.089	.081
193.954	337.220	13.412	13.495	.083
199.558	347.294	13.844	13.928	.084
206.054	359.060	14.343	14.432	.089
211.528	368.953	14.764	14.867	.093
216.440	377.826	15.142	15.237	.095
221.858	387.562	15.560	15.655	.095
229.601	401.419	16.158	16.249	.091
235.598	412.367	16.623	16.719	.096
241.028	422.258	17.045	17.143	.098
247.436	433.800	17.541	17.638	.097
253.704	445.267	18.028	18.130	.102
259.786	456.286	18.500	18.603	.103
266.086	467.817	19.991	19.097	.106
273.143	480.643	19.539	19.648	.109
280.176	493.442	20.086	20.197	.111
287.634	506.906	20.666	20.774	.108
294.927	520.052	21.232	21.338	.106
304.148	536.832	21.947	22.058	.111
310.397	548.152	22.432	22.544	.112
316.596	559.336	22.916	23.023	.107
321.271	568.051	23.282	23.397	.115
327.148	578.528	23.742	23.846	.104
333.661	590.661	24.251	24.367	.116
339.664	601.596	24.719	24.836	.117
346.557	614.004	25.254	25.369	.115
352.878	625.510	25.746	25.862	.116
359.986	638.526	26.299	26.421	.122
365.080	647.833	26.697	26.820	.123
371.811	660.071	27.225	27.345	.120
382.770	680.149	28.087	28.206	.119

We can discuss the comparison of these thermometers in two ways; either by direct comparison at the points we desire, or by the representation of the differences by a formula.

\* Evidently a mistake in the readings.

Joule's result in 1850 was referred to water at about 14° C., and in 1878 to water at 16°.5 C. Taking intervals in the above table of from 6° to 12°, so that the mean shall be nearly 14° and 16°.5, I find the following for the ratios:—

	1.0044	1.0042
	1.0042	1.0042
	1.0049	1.0040
	1.0047	1.0030
	1.0047	1.0035
	1.0052	1.0035
Mean,	<u>1.0047</u>	<u>1.0037</u>

So that we have the following for Joule's old and new values:—

	Old.	New.
	423.9	423.9
Correction for thermometer	2.0	1.6
“ “ latitude	.5	.5
“ “ sp. ht. of copper	.7	
	<u>427.1</u>	<u>426.0</u>
My value	427.7	427.1
Difference	.6	1.1

or 1 in 700 and 1 in 390 respectively.

But the correction found in this way is subject to local irregularities, and it is perhaps better in many respects to get the equation giving the temperature of Joule's thermometer on the air thermometer. Let  $T$  be the temperature by Joule's thermometer, and  $t$  that by the air thermometer. Then I have found

$$t = 0.002 + 1.00125 T - .00013 \{100 - T\} \{1 - .003(100 + T)\}$$

The factor 1.00125 enters in the formula, probably because the thermometer which Joule used to get the value of the divisions of his thermometer was not of the same kind of glass as his standard. The relative error at any point due to using the mercurial rather than the air thermometer will then be

$$E = 1 - \frac{dt}{dT} = -.00125 + .00000039 \{23300 - 666t + 3t^2\}$$

From this I have constructed the following table.

Temperature.	R.	Approximate Addition to Equivalent as measured on Joule's Thermometer.	
		Metric System.	English System.
0	.0078	3.3	6.0
5	.0066	2.8	5.1
10	.0054	2.3	4.2
15	.0042	1.8	3.2
20	.0031	1.3	2.4
25	.0021	.9	1.6
30	.0011	.5	.8

Corrected in this way we have, —

	Old.	New.
Joule's value	423.9	423.9
Reduction to air thermometer	1.9	1.7
“ latitude of Baltimore	.5	.5
Correction for sp. ht. of copper	.7	
	<hr/> 427.0	<hr/> 426.1
My value	427.7	427.1
Difference	<hr/> .7	<hr/> 1.0

or 1 in 600 and 1 in 426 respectively.

But it is evident that all the other temperatures used in the experiment must also be corrected, and I have done this in the following manner. The principal other correction required is in the capacity of the calorimeter, and this amounts to considerable in the experiments on mercury and cast-iron, where no water is used. Dr. Joule informs me that the thermometer with which he compared mine was made in 1844, but does not give any mark by which to designate it, although it is evidently the thermometer called “A” by him. I shall commence with the experiments of 1847. The calorimeter was composed of the following substances, whose capacities I recompute according to what in my paper I have considered the most probable specific heats.

	Weight.	Capacity according to Joule.	Most probable Specific Heat.	Most probable Capacity.
Water	77617 grains	77617	1.000	77617
Brass	24800 “	2319	.0900	2232
Copper	11237 “	1056	.0922	1036
Tin	(?)	363	. . .	363
Total capacity		81355		81248

Equivalent found	781.5 at about 59° F.
Correction for thermometer	3.3
“ “ capacity	1.3
“ “ latitude	.9
Corrected value	<u>787.0</u>

or 442.8 at 15° C. on the air thermometer.

The other experiment, on sperm oil, made at this time, is probably hardly worth reducing. The experiments of 1850 are of the highest importance, and should be accurately reduced.

In the experiments with water the capacity of the calorimeter is corrected as follows:—

	Weight.	Capacity used by Joule.	Most probable Specific Heat.	Most probable Capacity.
Water	93229.7	93229.7	1.000	93229.7
Copper	25541.	2430.2	.092	2349.8
Brass	18901.	1800.0	.091	1720.0
Brass stopper . . . .		10.3	. . .	10.3
Total capacity		<u>97470.2</u>		<u>97309.8</u>

Therefore correction is .0016.

Hence the result with water requires the following corrections:—

Joule's value	772.7 at 14° C.
Correction for thermometer	3.2
“ “ latitude	.9
“ “ capacity	1.2
	<u>778.0</u>

or 426.8 on the air thermometer in the latitude of Baltimore at the temperature of 14° C., nearly.

In the next experiment, with mercury, Joule determined the capacity of the apparatus by experiment. The mean of the experiments was that the apparatus lost 20°.33155 F. in heating 143430 grains of water 3°.13305 F. To reduce these to the air thermometer we must divide respectively by 1.0042 and 1.0056. Therefore the capacity must be divided by 1.0014. Therefore the corrected values are:—

	772.8 at 9° C.	775.4 at 11° C.
Correction for thermometer	4.4	4.0
“ “ capacity	1.1	1.1
“ “ latitude	.9	.9
	<u>779.2</u>	<u>781.4</u>

The reduction to the air thermometer was made for the temperatures of  $9^{\circ}$  C. and  $11^{\circ}$  C. respectively, but they both refer to the temperature of the water used when the capacity was determined; this was about  $9^{\circ}$  C. Hence these experiments gave 427.5 and 428.7 on the air thermometer, with the water at about  $9^{\circ}$  C.

The next experiments, with cast-iron, can be corrected in the same manner, and thus become

	776.0	773.9
Correction for thermometer	4.2	4.3
“ “ capacity	1.1	1.1
“ “ latitude	.9	.9
	<u>782.2</u>	<u>780.2</u>

and these are as before for water at  $9^{\circ}$ .

The determination by the heating of a wire, whose resistance was measured in ohms, can be thus reduced. The value found by Joule was 429.9 in the latitude of Baltimore at  $18^{\circ}.6$  C.

Using the capacity of the copper .0922, as I have done in my paper, this quantity will be increased to 430.3. But I have given reasons in my paper on the “Absolute Unit of Electrical Resistance” to show that there should be a correction to the B. A. Committee’s experiments, which would make the ohm .993 earth quadrant  $\div$  second, instead of 1.000 as it was meant to be, which nearly agrees with the quantity which I found, namely, .991. Taking my value .9911, Joule’s result will reduce as follows:—

	429.9 at $18^{\circ}.6$ C.
Correction for thermometer	+ 1.5
“ “ capacity	+ .4
“ “ ohm	— 3.8
Corrected value	<u>428.0 at <math>18^{\circ}.6</math> C.</u>

The last determinations in the “Philosophical Transactions” of 1878 can be reduced as follows.

The capacity of the calorimeter was determined by experiment, instead of calculated from the specific heat of copper given by Regnault, as in the older experiments. The value used, 4842.4 grains, corresponded to a specific heat of brass of about .090, which is almost exactly what I have considered right. The reduction to the air thermometer will decrease it somewhat, and the correction for the increase of the specific heat of brass and the decrease of the specific heat of water will also change it somewhat. In all, the amount will be about 1 in 200. Hence the reduction becomes as follows:—

Joule's values	772.7	774.6	773.1	767.0	774.0
Correction for thermometer	3.2	3.7	3.1	3.3	2.8
“ “ capacity	.2	.2	.2	.2	.2
“ “ latitude	.9	.9	.9	.9	.9
“ to vacuum	— .9	— .9	— .9	— .9	— .9
Corrected values	776.1	778.5	776.4	770.5	777.0
	at 14°.7	at 12°.7	at 12°.5	at 14°.5	at 17°.3

To reduce the values in English measure to meters and the Centigrade scale, I have simply taken the reducing factor  $1.8 \times .304794$ , although the barometer on the two systems is not exactly the same: for this is taken into account in the comparison of the thermometers. However, a barometer at 30 in. and 60° F. is equivalent to 759.86 mm. at 0° C. which hardly makes a difference of 0°.01 C. in the temperature of the hundred-degree point.

No.	Date.	Method.	Tem. of water.	Joule's Value.	Joule's Value re- duced to Air Ther- mometer and Lat- itude of Baltimore.		Rowland's Value.	J. — R.	Estimated weight.
					English measure.	Metric system.			
1	1847	Friction of water	15	781.5	787.0	442.8	427.4	+15.4	0
2	1850	“ water	14	772.7	778.0	426.8	427.7	— .9	10
3	“	“ mercury	9	772.8	779.2	427.5	428.8	— 1.3	2
4	“	“ mercury	9	775.4	781.4	428.7	428.8	— .1	2
5	“	“ iron	9	776.0	782.2	429.1	428.8	+ .3	1
6	“	“ iron	9	773.9	780.2	428.0	428.8	— .8	1
7	1867	Electric heating	18.6	....	....	428.0	426.7	+ 1.3	3
8	1878	Friction of water	14.7	772.7	776.1	425.8	427.6	— 1.8	2
9	“	“ “	12.7	774.6	778.5	427.1	428.0	— .9	3
10	“	“ “	15.6	773.1	776.4	426.0	427.3	— 1.3	6
11	“	“ “	14.5	767.0	770.5	422.7	427.5	— 4.8	1
12	“	“ “	17.3	774.0	777.0	426.3	426.9	— .6	1

In combining these so as to get at the true difference of Joule's and my result, we must give these different determinations weights according to their respective accuracy, especially as some of the results, as No. 11, have very little weight. Joule rejected quite a number of his results, but I have thought it best to include them, giving them small weights, however. In this way we obtain a value for Joule's experiment of 426.75 at 14°.6, my value at this point being 427.52. The difference amounts to 1 in 550 only. Giving the observations equal weights, this would have been 1 in 430 nearly. The quantity 426.75 is what I find at 18° C. So that my result at this particular temperature differs from that of Joule only the amount that water changes in specific heat in 3°.4 C.



Joule's value is *less* than my value to the amount given, but the value from the properties of air, 430.7 at 14° C. is greater, although the method can have little weight.

It might be well to diminish my values by 1 part in 1000 so as to make them represent the mean of Joule's and my own experiments. It is seen that the experiment by the method of electric heating agrees very exactly with the other experiments, *because I have reduced it to my value of the ohm*. Hence I regard it as a very excellent confirmation of my value of that unit.

BALTIMORE, Feb. 16, 1880.

## III.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF HARVARD COLLEGE, UNDER THE DIRECTION OF PROFESSOR JOHN TROWBRIDGE.

NO. XXIII.—THE MAGNETIC MOMENT OF FLEITMAN'S NICKEL.

BY J. E. BULLARD.

Presented June 9, 1880.

IN March, 1879, H. Th. Fleitman published, in the *Berichte der Deutschen Chemischen Gesellschaft*, No. 5, 1879, p. 454, a paper on nickel, in which he stated that the porosity of nickel was caused by an absorption of carbonic acid in melting, and that the addition of a small portion of magnesium in the metal bath would prevent this absorption. The addition of even one eighth per cent. of magnesium entirely changed the structure of the nickel; it became very ductile and malleable, took a high polish, and resisted the action of the air.

As this discovery is of very great importance in the arts, I have endeavored to ascertain whether the magnetic properties of the nickel are changed by the addition of the magnesium which causes such changes in the mechanical properties of the metal.

The apparatus used was an ordinary telescope and scale, and a magnetometer. A short cylindrical bar of Fleitman's nickel, fully magnetized, was placed before the magnetometer. The method used was the observation of deflections, using the formula  $M = \frac{1}{2} r^3 T \tan \phi$ .  $M$  is the magnetic moment of the bar;  $T$  is the horizontal intensity of terrestrial magnetism;  $r$  is the distance of the centre of the magnet from the mirror of the magnetometer, in millimeters; and  $\phi$  is the deflection of the mirror caused by the magnet. In the present case,—

The length of the bar of nickel was 67 mm. and its diameter 6 mm.

$r = 277.5$  mm.,

$T$  (for Cambridge)  $= 1.65$ ,

and  $\log \tan \phi = 9.6882$ .

Hence  $M$  is found to be 8,600,000.

A bar of stub steel, of the same dimensions, was found to have a magnetic moment of 8,750,000. This variety of steel is used for the common grade of tools, and is comparatively soft. The magnetic moment of a bar of ordinary cast nickel was then obtained. Both bars were highly tempered to render the conditions of comparison as nearly equal as possible.

With the same formula the magnetic moment of a bar of cast nickel was found to be only 36,330; that is, about one two-hundred-and-twentieth as much as the moment of Fleitman's nickel.

These numbers are, of course, not perfectly exact, for the changes of magnetism in bars from time to time preclude perfect exactness; still the relation of the magnetic moments may be considered very accurate.

This result is certainly surprising; that the addition of  $\frac{1}{2}$  per cent of magnesium to a bar of nickel should increase the magnetism 220 times shows that change of structure in a metal increases its magnetic capacity.

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#### No. XXIV.—THERMAL CONDUCTIVITY OF GLASS AND SAND.

By C. B. PENROSE.

Presented June 9, 1880.

IN determining the conductivity of glass I used the same method that Forbes employed in determining the conductivity of iron.

A bar of glass is maintained, at one end, at a constant temperature. When the bar has reached a permanent state of heat, that is, when the amount of heat received by any portion exactly equals the amount given out by that portion, the temperature of a number of points on the bar are determined. The bar is taken so long that the heat at the heated end will not be sufficient to raise the temperature of the other end above that of the air. The temperatures determined are laid off as ordinates, the abscissas being the corresponding lengths of the bar. The equation of the curve thus formed can be determined. Then an exactly similar bar to the preceding is heated to a known temperature, and as it cools the temperatures are taken every minute, and thus the loss of temperature per minute is determined.

These diminutions of temperature, each corresponding to a known temperature of the bar, are laid off as ordinates of a second curve, each ordinate corresponding to an ordinate of the first curve, which expresses the temperature of the bar at any point. Thus every ordinate of the second curve will give the loss of temperature per minute, from that portion of the bar which is at the temperature given by the corresponding ordinate of the first curve. And the area of a definite portion of the second curve multiplied by the specific heat of the glass gives the amount of heat lost from a corresponding definite portion of the bar, in unit of time.

If we have a vertical section of any substance, of thickness  $x$ , one face at the constant temperature  $t_0$  and the other at the temperature  $t$ , and  $k$  = the conductivity of the substance, the quantity of heat that passes through an area  $A$  in unit time =  $Q$ , where

$$Q = K \cdot A \frac{t_0 - t}{x}. \quad \therefore K = \frac{Q}{A} \frac{1}{\frac{t_0 - t}{x}}.$$

If the section is an infinitely thin lamina of thickness  $d x$ , and if  $d t$  = the difference of temperature of the two sides, —

$$K = \frac{Q}{A} \frac{1}{\frac{d t}{d x}} =, \text{ at the limit, } \frac{Q}{A} \frac{1}{D_x t}.$$

$D_x t$  can be found for any point of the bar, by finding the tangent at the corresponding point of the first curve. Hence if  $A$  = area of cross-section of bar,  $S$  = the specific heat of the glass, and "area" = the area of the second curve beyond the point in question, the conductivity at that point is  $K = \frac{S \text{ area}}{A D_x t}$ .

The area of the second curve beyond the point in question, multiplied by  $S$ , evidently equals the whole amount of heat that passes, in unit time, through the section of the bar at that point; for the end of the bar is at the same temperature as the air.

I used a bar of flint glass, about 30 cm. long and 1.1 cm. in diameter. One end was inserted in the side of a metallic vessel, and heated to 100° by boiling water. The other end was supported on a piece of wood. Two screens of card-board were placed in front of the can and lamp to prevent the bar being heated by radiation. Seven points were marked on the bar: the first, 3 centimeters from the can, and the others, 1, 2, 3, 5, 7, and 9 centimeters from the first point. The temperatures were measured by a thermopile made by a junction of copper and iron wires, fastened like two links of a chain, so that they

could be placed astraddle the bar, and thus make a very close connection.

After the water had boiled one hour the bar reached a permanent state. I then took the following observations of the temperatures of the different points, as shown by the deflections of the galvanometer. The temperatures are expressed in centimeters of the galvanometer scale, and consequently give the excess of the temperatures above that of the air.

1st pt.	2d pt.	3d pt.	4th pt.	5th pt.	6th pt.	7th pt.
7.2	4.9	2.9	2.3	1.4	1.0	0.4
7.2	4.9	2.9	2.2	1.4	1.0	0.4
8.2	4.9	3.2	2.3	1.7	1.1	0.4
7.9	4.7	2.9	2.0	1.4	0.9	0.4
6.9	4.2	2.7	1.9	1.4	1.2	0.4
7.7	5.0	3.0	1.9	1.4	0.9	0.4
7.1	4.4	2.8	2.2	1.3	0.9	0.7
Average value, } 7.45	4.71	2.91	2.11	1.43	1.0	0.44

These average values are laid off as ordinates of a certain curve whose abscissas are the corresponding lengths of the bar. We can find an equation to satisfy these seven known points of the form:—

$$y = Ax^6 + Bx^5 + Cx^4 + Dx^3 + Ex^2 + Fx + G.$$

In drawing the curve I found that the sixth point would not come in the symmetrical curve, and so I threw it out; thus we shall have a curve of the fifth degree, the constants of whose equation can be determined from the following equations:—

$$y = Ax^5 + Bx^4 + Cx^3 + Dx^2 + Ex + F \quad \text{Eq. (1)}$$

$$F = 7.4.$$

$$4.7 = A + B + C + D + E + F.$$

$$2.9 = 32A + 16B + 8C + 4D + 2E + F.$$

$$2.1 = 243A + 81B + 27C + 9D + 3E + F.$$

$$1.4 = 3125A + 625B + 125C + 25D + 5E + F.$$

$$0.4 = 6561 \times 9A + 6561B + 729C + 81D + 9E + F.$$

Solving these equations, we find the coefficients  $A B C D E F$ , and substituting in Eq. (1), we get the equation of the first curve:—

$$y = -.000238x^5 + .00598x^4 - .0799x^3 + .701x^2 - 3.326x + 7.4.$$

The next step is to determine the second curve, or the rate of cool-  
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ing. I took a piece of the bar used in the preceding experiment, and heated it in boiling water for twenty minutes. The rod was then taken out, wiped dry, placed horizontally across two wooden props, and the thermo-electric junction of copper and iron was placed upon the centre in a deep groove to insure a close connection. As the bar cooled the deflections on the galvanometer scale were read every minute. I performed the experiment four times, but the results were so nearly alike that I take only the last. The following numbers give the excesses of temperature above that of the air every minute:—

8.2	1.2	3.1	0.5	1.2	0.2	0.6	0.1
7.0	1.1	2.6	0.3	1.0	0.1	0.5	0.1
5.9	1.0	2.3	0.3	1.9	0.1	0.4	0.1
4.9	0.8	2.0	0.3	0.8	0.1	0.3	0.1
4.1	0.5	1.7	0.2	0.7	0.1	0.2	0.1
3.6	0.4	1.5	0.3				

From these numbers we see that if any portion of the bar is at the temperature 8.2 it loses 1.2 units of temperature in one minute, etc. If these losses are laid off as ordinates right below the corresponding temperature, (as given by the ordinates of the first curve,) we shall have the second curve, whose area, for any definite portion, represents the loss of temperature per minute from a corresponding portion of the bar. If this second curve is drawn on co-ordinate paper, its area can be found by actual measurement, and we need not obtain its equation. The errors of such a method of measurement will be no greater than those which are liable to enter as experimental errors.

Making the measurement in the manner indicated above, and using the equation,  $K = \frac{S \text{ area}}{A D_x t}$ ,

$$\text{I found for point 2, } K = .2 \frac{1.97}{2.14} = .18.$$

$$\text{For point 3, } K = .2 \frac{1.38}{1.31} = .21.$$

$$\text{For point 4, } K = .2 \frac{1.05}{0.73} = .28.$$

From these results it appears that the conductivity decreases as the temperature increases. It has also been shown, by Forbes, that the conductivity of iron decreases as the temperature increases.

The units in which the preceding conductivities are expressed are the centimeter, the minute, a centimeter deflection on the galvanometer scale, and the unit of heat is the amount of heat required to raise the temperature of 1 cm.<sup>3</sup> of the glass one unit of deflection. To compare these conductivities with those determined by Forbes for iron, we must reduce them to functions of the units: the foot, the centigrade degree, and the minute.

$S$  and  $D_{\theta}t$  are ratios, and are independent of units.  $A$  contains cm.<sup>2</sup> and "area" contains cm.<sup>3</sup>

$$1 \text{ cm.}^2 = .155 \text{ sq. in.} = .00107 \text{ sq. ft.}$$

$$1 \text{ cm.}^3 = .061 \text{ cu. in.} = .000035 \text{ cu. ft.}$$

In determining the relation between one degree centigrade and one unit deflection, I made four measurements, using heated sand, the thermometer and thermopile being buried side by side.

5.5 cm.	corresponds to a rise in temp. of	12.0°
8.5	"	16.3
5.0	"	10.8
6.7	"	14.2

From these results, evidently,

1 cm.	corresponds to a rise in temp. of	2.18°
1	"	1.91
1	"	2.16
1	"	2.11
		4)8.36
Average	. . . . .	2.09

Hence, to reduce  $K$  to the required system of units, we divide by 2.09 and .00107 and multiply by .000035, or we multiply by .015.

The conductivities determined before become in the new system of units,

$$K = .00270.$$

$$K = .00315.$$

$$K = .00420.$$

These results can be summed up as follows. The numbers in the first row give, in centigrade degrees, the excess of the temperature of the bar above that of the air, and the second row the corresponding conductivities. The air was about 21° C.

Temperature of bar . .	19°.8	6°.08	4°.4
Conductivity . . . .	.00270	.00315	.00420

The conductivity of iron, as determined by Forbes, varied from .01337 at 0° C. to .00801 at 275° C. And the conductivity of sandstone, determined by burying thermometers from three to twenty-four feet below the surface, was found to be .000689.

The conductivity which I found for glass, therefore, lies between that of iron and that of sandstone. It also, like the conductivity of iron, increases as the temperature decreases. It has not been determined how the conductivity of sandstone varies with the temperature.

#### *Conductivity of Sand.*

To determine the conductivity of sand I used the following method. The sand is put in a thin metallic vessel; inside of this is put an exactly similar smaller metal vessel, which rests on the bottom of the outer one. Thus the sand forms a layer, protected on each side by the thin metal. These two vessels are entirely immersed in a larger vessel containing a known volume of water. The interior of the inner vessel is kept at a constant temperature (by means of steam). With a thermometer we can find the temperature of the outside water every minute, and thus construct a curve; the abscissas being the times and the ordinates the corresponding temperatures. In the next place, fill the outside vessel with the same volume of water used in the preceding experiment, heat it to a known temperature, and find the rate at which it cools. For this purpose we construct a second curve, having the times for abscissas and the temperatures for ordinates. Take any ordinate  $t$ , of the first curve, and let  $d t_1 =$  the gain of temperature in time  $d T$ ; then, if  $V =$  the volume of the water,  $d t_1 \cdot V =$  the amount of heat gained in time  $d T$ . Take the same ordinate  $t$ , of the second curve, and let  $d t_2 =$  the loss of temperature in time  $d T$ , then  $d t_2 \cdot V =$  the loss of heat from the water, when the temperature is  $t$ , in time  $d T$ . Hence the whole amount of heat that passes through the layer of sand in time  $d T = Q = d t_1 \cdot V + d t_2 \cdot V$ .

The formula for the quantity of heat that passes, in time  $T$ , through a section of thickness  $x$ , and area  $A$ , is  $Q = K \cdot A \cdot \frac{t_0 - t}{x} T$ . In the present case  $T = d T$ , and we have found the value for  $Q$ ,

$$d t_1 \cdot V + d t_2 \cdot V = K \cdot A \cdot \frac{t_0 - t}{x} d T;$$



$$\therefore V \left[ \frac{d t_1}{d T} + \frac{d t_2}{d T} \right] = K \cdot A \frac{t_0 - t}{x}.$$

At the limit we find the quantity of heat that passes through when the temperature of the water is  $t$

$$= V (D_T t_1 + D_T t_2) = K \cdot A \frac{t_0 - t}{x}.$$

From the first and second curve  $D_T t_1$  and  $D_T t_2$  are easily obtained, and as all the other quantities are known,  $K$  can be determined.

In my experiment I used for the outer vessel a tin can 7.1 cm. in height. This was covered with the exception of a hole in the top, around which was a collar. In this hole was placed a large test-tube of glass which just fitted the hole. The space between the test-tube and the walls of the can was filled with sand. This was placed in a larger tin can almost full of water, and suspended about 4 cm. from the bottom by a string. Steam was passed from a retort into the test-tube, and several times during the experiments I placed a thermometer in the test-tube, and it always showed that the temperature was  $100^\circ \text{C}$ .

At the start the water was  $23.3^\circ$ . I took down the temperatures every minute for almost an hour, but as I do not use these in constructing the curve, I give only the temperature determined every five minutes, after the first hour:—

Temperature.	Excess above $23^\circ.3$ .	Temperature.	Excess above $23^\circ.3$ .
29.4	6.1	34.0	10.7
30.1	6.8	34.3	11.0
30.7	7.4	34.6	11.3
31.3	8.0	34.9	11.6
31.8	8.5	35.1	11.8
32.3	9.0	35.3	12.0
32.8	9.5	35.5	12.2
33.3	10.0	35.7	12.4
33.6	10.3	35.9	12.6

The temperature of the air was  $23.3^\circ$ . The curve given by these points is not very regular; it changes several times from concave to convex. I therefore determined to take a small arc, find its equation, and investigate the conductivity as given by this arc. I considered only the points

7.4, 8.0, 8.5, 9.0, 9.5, 10.0.

If five small divisions of the co-ordinate paper are taken as one unit, an equation of the fifth degree, satisfying these six points, is found from:—

$$1.6 = A + B + C + D + E + F. \quad F = 1.48.$$

$$1.7 = 32 A + 16 B + 8 C + 4 D + 2 E + F.$$

$$1.8 = 243 A + 81 B + 27 C + 9 D + 3 E + F.$$

$$1.9 = 1024 A + 256 B + 64 C + 16 D + 4 E + F.$$

$$2.0 = 3125 A + 625 B + 125 C + 25 D + 5 E + F.$$

From these equations  $A B C D E F$  are found, and the required equation is:—

$$y = -0.0005 x^4 + 0.006 x^3 - 0.0245 x^2 + 0.139 x + 1.48.$$

Next, the same volume of water used in the preceding experiment was heated to  $36^\circ$ . The can was then placed on the same wooden props used before, and by means of the same thermometer the temperatures were read off every five minutes. The temperature of the air and of the water at starting was  $23^\circ$ . The following were the temperatures every five minutes:—

Temperature.	Excess above Air.	Temperature.	Excess above Air.
$36.0$	$13.0$	$32.1$	$9.1$
$35.3$	$12.3$	$31.5$	$8.5$
$34.5$	$11.5$	$30.9$	$7.9$
$33.7$	$10.7$	$30.3$	$7.3$
$32.8$	$9.8$		

I consider here only the temperatures included by the first equation; that is, from 9.8 to 7.3.

The equation of this second curve is found by the same process as in the first curve to be  $y = 0.12 x + 1.46$ ; therefore, the curve is a right line. The thickness of the layer of sand was 2.7 cm. =  $x$ . To determine  $A$ , I took the mean radius of the layer = 1.35 cm.

$$\therefore A = 2 \pi \cdot 1.35, 7.1 = 60.21 \text{ cm.}^2$$

$$h = \text{height of the can} = 7.1 \text{ cm.}$$

$V$  = volume of water. The water weighed 906 grammes; therefore, its volume was 906 cm.<sup>3</sup>

$$\frac{V}{A} x \text{ is constant, and} = 40.62.$$

$$\therefore K = 40.62 (D_T t_1 + D_T t_2) \frac{1}{t_0 - t}.$$

$$D_T t_1 = [D_x y] \text{ and } D_T t_2 \text{ always} = .12.$$

$$[D_x y]_{x=0} = 0.139; \therefore D_T t_1 + D_T t_2 = .259,$$

$$\text{and } t_0 - t = 100 - 30.7 = 69.3;$$

$$\therefore K = .1518.$$

$$[D_x y]_{x=1} = .106; \quad \therefore D_T t_1 + D_T t_2 = .226, \\ \text{and } t_0 - t = 100 - 31.3 = 68.7; \\ \therefore K = .1336.$$

$$[D_x y]_{x=2} = 0.097; \quad \therefore D_T t_1 + D_T t_2 = .217, \\ \text{and } t_0 - t = 100 - 31.8 = 68.2; \\ \therefore K = .1292.$$

$$[D_x y]_{x=3} = 0.100; \quad \therefore D_T t_1 + D_T t_2 = .22, \\ \text{and } t_0 - t = 100 - 32.3 = 67.7; \\ \therefore K = .132.$$

$$[D_x y]_{x=4} = .103; \quad \therefore D_T t_1 + D_T t_2 = .233, \\ \text{and } t_0 - t = 100 - 32.8 = 67.2; \\ \therefore K = .1348.$$

$$[D_x y]_{x=5} = .094; \quad \therefore D_T t_1 + D_T t_2 = .214, \\ \text{and } t_0 - t = 100 - 33.3 = 66.7; \\ \therefore K = .1303.$$

The average value of  $K$  is found, from the above observations, to be  $K = .1353$ .

The conductivities determined above should all be the same, and they are almost exactly the same, except the first; for after the first hour the sand must have reached a permanent state of heat, and the mean temperature was sensibly the same for all the values of  $K$ ; the water only gained  $2^\circ.6$  of temperature. Consequently, from these results it cannot be determined whether the conductivity of sand increases or decreases as the temperature increases. But to find how the conductivity varies with the temperature, the value of  $t_0$  should be changed; therefore the temperature in the test-tube should be varied.

To reduce the average value of  $K$  to the same units used in glass, we multiply by .000035 and .0328 and divide by .00107, or we merely multiply by .00107 and find as the value of  $K$ , .000144771.

Forbes determined the conductivity of sand by burying thermometers below the surface (3 — 25 ft.), and found it to be .000169. The temperature of the sand for Forbes's conductivity was about  $62^\circ \text{ F.} = 34^\circ.4 \text{ C.}$  The mean temperature of the sand in my experiment was about  $50^\circ \text{ C.}$  From this it is probable that the conductivity of sand, like that of glass and of iron, decreases as the temperature increases. The specific gravity of the sand in my experiment was 16.

The errors arising from values of  $D_x y$  are probably not very large. The arc of the first curve is almost a straight line, and the values of

$D, y$  — after the first — were found to be almost the same. To obtain an absolutely reliable equation, it is necessary to take a great many points very near together; and as each point raises the equation one degree, and adds one more equation to those from which the coefficients are found, the mere mechanical work of finding the equation of the curve becomes very great.

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## NO. XXV. — EFFECT OF THE TENSION OF MEMBRANES ON SOUND.

BY G. F. HARTSHORN.

Presented June 9, 1880.

SEVERAL experiments were tried bearing upon this subject by speaking alternately through two telephones, the mouth of one being covered with a membrane and the mouth of the other being open, the difference in sound between the two being observed by means of a telephone in the circuit. These experiments were not thought trustworthy, as it was difficult to speak with equal intensity and at precisely the same distances from the two instruments; to obviate these difficulties the following apparatus was devised.

An ordinary Bell telephone was provided with two tubes, which were placed opposite to each other on opposite sides of the vibrating plate. Rubber tubes were slipped upon these two tubes and led away to a mouth-piece which consisted of a chamber of clay, so moulded as to allow the extremities of the rubber tubes to terminate in broad glass funnels which were imbedded at a certain angle with each other in the clay. Another telephone was included in the circuit to enable one to hear what was transmitted.

Sounds sent to the telephones by both the mouth-pieces in the clay chamber would not be heard at the receiving telephone, because the equal vibrations striking opposite sides of the sending telephone plate would neutralize each other, but by closing alternately the connecting tubes the sound can be passed at will through either of the mouth-pieces.

In experimenting with the voice it was found that, with both a loose and a tight membrane, the articulation was plainer, and the sounds somewhat louder, than when passed through the open mouth-piece.

It was also noticed that the vowels were broadened,  $\tilde{a}$  becoming  $\bar{a}$ , etc., the effect of the tight membrane in both cases being the strongest.

Musical sounds passed through a tight membrane appeared much louder, and those of the highest pitch much more intense, than when passed through the open mouth-piece. While experimenting with sounds of a low pitch passed through a tight membrane, it was noticed that, while the fundamental tone was hardly perceptible, the first harmonics could be plainly heard. This fact seems to have the following explanation: the membrane being found to be much more sensitive to sounds of a higher pitch than to those of a lower, when the low tone was sounded the membrane transmitted the vibrations of the harmonics sounding with it, of a higher pitch than the fundamental tone, before the fundamental tone itself. Without the membrane no such effect was produced. Loose membranes gave the same effect, though relatively to the experiments with the voice much less intense, being weaker than the sound transmitted through the open mouth-piece.

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While trying the above experiments the idea suggested itself that two telephones placed end to end, having one diaphragm in common and furnished with two mouth-pieces connected by long tubes, would furnish an instrument for measuring reflected sound. Such an instrument could be used as follows. Place one of the mouth-pieces to receive the direct and the other the reflected sound. Now, if the two sounds were equal, nothing would be heard at the telephone placed in the circuit for the observer, as proved by the result of the experiment made in transmitting one sound through two mouth-pieces. If one sound was stronger than the other, its vibrations would be transmitted, and it would be heard.

If a thumb-screw with a scale be fitted on the tube through which the stronger sound passes, by compressing the tube by means of the screw the intensity of the sound can be graduated till nothing is heard by the observer, thus proving the two to be equal.

Reading the number of turns from the scale, the relative intensities of the two sounds can be measured, and if the scale be made so that a certain number of turns equals a sound of a certain intensity, the measurement becomes positive instead of relative.

## No. XXVI.—A PHENOMENON OF ELECTRICAL CONVECTION.

BY JAMES JAY GREENOUGH.

Presented June 9, 1880.

WHILE studying the spectra formed by passing a spark from an induction coil through heated media, I perceived that, when the negative terminal consisted of a very fine platinum wire, the passage of the sparks made it glow, and soon fused it. Supposing that the heating effect was due to the resistance offered by the fine platinum wire, I joined the two terminals and allowed the induced current to flow through the circuit uninterrupted. No heating effect was produced. The phenomena is a very marked one, and the incandescence of the platinum gives a brilliant star of light.

This effect seems to be due to the impact of the particles of matter upon the negative terminal, and is related to the electrical convection effects first studied by Prof. Rowland. It can also be termed a Crookes effect under ordinary atmospheric pressure, for the electrified stream of molecules urged with great energy, rebound from the point of the negative terminal, and, being confined by the stratum of gases, expend their *vis viva* in repeated blows upon the terminal, which is raised thereby to incandescence.

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## No. XXVII.—THE EARTH AS A CONDUCTOR OF ELECTRICITY.

BY JOHN TROWBRIDGE.

Presented June 9, 1880.

THE Observatory of Harvard University transmits time signals from Cambridge to Boston, a distance of four miles. The regular recurrence of the beats of the clock at the Observatory affords a good means of studying the spreading of the electrical current from the terminal of the battery, which is grounded at the Observatory; and the establishment of the telephone dispatch companies in Boston and Cambridge, with their various ground connections, gave me unusual means of studying this spreading.

In all the telephone circuits between Boston and Cambridge, and

in Cambridge alone, in the neighborhood of the direct line between Boston and Cambridge, the ticking of the Observatory clock can be heard. This transmission of the time signals to the various telephone stations has been attributed to the proximity of the telephone circuit wires to the time wires from the Observatory. This is evidently an erroneous conclusion, as will be seen from a short mathematical consideration.

The expression for the induction produced in one wire by making and breaking a current in a parallel wire\* is  $R_2 y_2 = \pm M y_1$ , in which  $y_2$  represents the induced current,  $R_2$  the resistance of the circuit which conveys this induced current,  $M$  the coefficient of induction between the parallel circuits, and  $y_1$  the current in the primary circuit, the interruption of which produces the induced currents.

Now  $M = \iint \frac{ds ds'}{r}$ , in which  $ds$  and  $ds'$  are elements of the parallel wires, and  $r$  is the perpendicular distance between them. The value of  $M$  in the case we are considering is  $M = \frac{A^2}{r}$ , in which  $A$  represents the length of the parallel wires, along which the induction takes place, and  $r$  is the distance between the wires. We shall therefore have

$$R_2 y_2 = \pm \frac{A^2}{r} y_1. \quad \text{Eq. (1)}$$

Now the electromotive force of the induced current  $y_2$  is very much greater than that of the inducing current  $y_1$ , and in order that the current strength  $y_2$  should be able to develop even a small electro-magnetic effect in the receiving telephone, the coefficient of induction  $\frac{A^2}{r}$  must be large, or in other words the distance along which the lines run parallel must be great, and the distance  $r$  between these lines must be small. An arithmetical consideration of Eq. (1) will convince one that, with telephones of the resistance usually employed (50 units) no inductive effect will be perceived, by the employment of even ten quart Bunsen cells, between wires which run parallel to each other a foot apart for the distance of thirty or forty feet. In order to detect an inductive effect under these conditions, a telephone of three or four units of resistance and a large battery must be employed. With a telephone of 30 or 40 units of resistance similar to those employed on district circuits, no induction can be perceived under the conditions we have prescribed.

For still stronger reasons it is impossible to hear telephonic messages

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\* Maxwell's Electricity and Magnetism, ii. 209.

by induction from one wire to another, unless the two wires between which induction is produced run parallel and very near to each other a long distance. This distance generally exceeds the distance at which the ordinary Bell telephone ceases to transmit articulate speech. The effects which have usually been attributed to induction on telephone circuits are due to the earth connections and to imperfect insulation. Indeed, there would be no trouble from induction if telephone wires were enclosed in a cable; for a consideration of Eq. (1) will make it evident that the telephonic messages transmitted over one wire, on account of the feeble currents which produce them, would have no practical effect upon the neighboring wires enclosed with it.

Since the transmission of the time signal service of Harvard College Observatory through all the telephone circuits in Boston and Cambridge is evidently not due to induction, but to tapping, so to speak, the earth at points which are not at the same electric potential, it was an interesting question to study the extent of the equipotential surfaces formed around the grounds of the time service circuit at Cambridge and in Boston. In this survey I was greatly assisted by Mr. G. H. Francis and Mr. H. C. French.

I speedily discovered that the time signals could be distinctly heard in a field an eighth of a mile from the Observatory, where one ground of the time circuit is located. The method of exploration consisted in running a wire five or six hundred feet along the grass, grounding its ends in moist earth, and including a telephone in the circuit. On completing the circuit through the telephone and the ground the evidence of an electrical current was plainly apparent from the ticking which making and breaking the circuit produced in the telephone, and the signals of the Observatory clock were distinctly heard. At the distance of a mile from the Observatory and not in the direct line between the Observatory and the Boston office, the time signals were obtained by tapping the earth at points only fifty feet apart. At a distance of five hundred feet directly behind the Observatory, no points five hundred feet apart could be found which were not practically at the same potential. The survey was carried to a distance of a mile behind the Observatory grounds with negative results. At points one mile from the central line between the Observatory and the Boston office the time signals could not be heard on the trial wire of six hundred feet. This was to be expected, since the trial wire should have its length increased as the distance from the grounds of the battery increases, in order to permit of one end of the wire touching a point of much higher potential than the other.



The theoretical possibility of telegraphing across large bodies of water is evident from this survey which I have undertaken. The practical possibility is another question. At no point in the survey did I find an absence of earth currents. The peculiar crackling noises heard in telephones are due to earth currents, and not to fluctuations in the batteries employed on telephone circuits; for they were characteristic of the circuits employed by me in which the earth was used as a part of the circuit, and were absent when a battery circuit was closed without the intervention of the earth. The tick produced in the exploring telephone whenever the circuit was closed through the ground was due to earth currents, and not to polarization between the copper wire and the wet earth; for it was many hundred times stronger than the polarization effects produced by dipping the copper terminals of the telephone wire in acidulated water. This crackling noise produced by the earth currents in a telephone is a curious phenomenon, and shows that the earth currents have a rapidly intermittent character which escapes observation by any other instrument. A delicate electro-dynamometer, for the registration and observation of these intermittent earth currents, is much to be desired. In some cases the pulsatory effect of these earth currents was very marked. At no point which I explored were evidences of earth currents absent.

In a discussion of the earth as a conductor Steinheil says: "We cannot conjure up gnomes at will, to convey our thoughts through the earth. Nature has prevented this. The spreading of the galvanic effect is proportional, not to the distance from the point of excitation, but to the square of this distance; at the distance of fifty meters only exceedingly small effects can be produced by the most powerful electrical effects at the point of excitation. Had we means which could stand in the same relation to electricity that the eyes stand to light, nothing would prevent our telegraphing through the earth without telegraph conductors, but it is not probable that we shall ever attain this end." \*

Theoretically, however, it is possible to-day to telegraph across the Atlantic Ocean without a cable. Powerful dynamo-electric machines could be placed at some point in Nova Scotia, having one end of their circuit grounded near them and the other end grounded in Florida, the conducting wire consisting of a wire of great conductivity, and being carefully insulated from the earth except at the two grounds. By exploring the coast of France, two points on two surfaces not at

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\* Dub. Anwendung des Elektromagnetismus, p. 172, 1873.

the same potential could be found, and by means of a telephone of low resistance the Morse signals sent from Nova Scotia to Florida could be heard in France. With the light of our present knowledge the expenditure of energy on the dynamo-electric engine would seem to be enormous.

The points made in this paper are as follows:—

1. Disturbances in telephone circuits usually attributed to effects of induction are, in general, due to contiguous grounds of battery circuits. A return wire is the only way to obviate these disturbances.

2. The well-defined equipotential surfaces in the neighborhood of battery grounds show the theoretical possibility of telegraphy across bodies of water without the employment of a cable, and leads us to greatly extend the practical limit set by Steinhilber.

3. Earth currents have an intermittent character, with periods of maxima and minima, which may occur several times a minute during the entire day.

## IV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.RESEARCHES ON THE SUBSTITUTED BENZYL COM-  
POUNDS.

## NINTH PAPER.

THE SYNTHESIS OF ANTHRACENE AND PHENANTHRENE  
FROM ORTHOBROMBENZYL BROMIDE.

BY C. LORING JACKSON AND J. FLEMING WHITE.

Presented May 14, 1879.

*Discovery of Anthracene.*

THE first notice of anthracene (under the name paranaphthaline) appears in a paper\* on compounds of hydrogen and carbon, published by Dumas and Laurent in 1832. They obtained it in the fractional distillation of coal-tar from the portions with the highest boiling-point, but did not succeed in purifying it, as is shown by the melting-point  $180^{\circ}$ , and the formula  $C_{15}H_6$ . Laurent,† in 1835, studied its oxidation product "paranaphthalese" (anthrachinone), and in 1837 ‡ proposed the name anthracene for it; but neither of these papers, nor one § also published by Laurent, in 1839, gives a satisfactory account of the hydrocarbon, as the quantity at his disposal was too small for complete purification.

The first accurate characterization of anthracene is due to Fritzsche,|| who, in 1857, obtained from coal-tar a hydrocarbon with the formula  $C_{14}H_{10}$ , and melting-point  $210^{\circ}$ , forming a picric acid compound melting at  $170^{\circ}$ , but he did not identify it with the anthracene of Laurent. This was reserved for Anderson,¶ who in 1861 re-

\* Ann. Chim. Phys., l. 187.

† Ibid., lx. 220.

‡ Ibid., lxvi. 149.

§ Ibid., lxxii. 415.

|| St. Petersburg Acad. Ber., 1857. Journ. pr. Ch., lxxiii. 286.

¶ Ann. Chem. Pharm., cxxii. 294.

peated Laurent's experiments on a larger scale, and showed that his anthracene had the formula  $C_{14}H_{10}$ , melted at  $213^{\circ}$ , and was the same as Fritzsche's unnamed hydrocarbon.

In 1867, Fritzsche\* described the preparation of his reagent (dinitroanthrachinone), and its use in the detection and purification of hydrocarbons; and Berthelot† reviewed all the previous work upon anthracene, determining its boiling-point  $360^{\circ}$  for the first time.

The next important paper on the subject appeared in 1869, when Fritzsche,‡ on account of its behavior with his reagent, pronounced anthracene a mixture of two very similar hydrocarbons, which he called photene, melting-point  $210^{\circ}$ – $212^{\circ}$ , and phosene, melting-point  $193^{\circ}$ .

In the following year (1870) general attention was attracted to anthracene by the appearance of Graebe and Liebermann's famous paper§ on anthracene and alizarine, in which they not only proved that alizarine was dioxyanthrachinone by preparing it synthetically from anthracene, but described a large number of derivatives of anthracene, giving for the first time the melting-point of anthrachinone  $273^{\circ}$ . They showed, too, that Fritzsche's photene was identical with anthracene, but were unable to obtain his phosene, which Barbier|| four years later showed was probably a mixture of anthracene and phenanthrene.

### *Syntheses of Anthracene.*

In describing the syntheses of anthracene, all those made by the same method will be grouped together, and these groups will be taken up in the order of their discovery.

1. Limpricht¶ was the first (in 1866) who made anthracene synthetically, unless, indeed, one of the products obtained by Märcker,\*\* in 1865, from the action of heat on tolallylsulphide must be considered anthracenesulphide, but there seems to be no sufficient ground for this supposition. Limpricht's method consisted in heating benzylchloride with water in a sealed tube to  $190^{\circ}$  for eight hours; the products were benzylether, an oil  $C_{14}H_{14}$ , and anthracene.

\* Zeit. für Chemie, 1867, p. 289.

† Bull. Chem. Soc., viii. 231.

‡ Zeit. für Chemie, 1869, p. 387.

§ Ann. Chem. Pharm., Supp., vii. 257. A preliminary notice appeared in 1868, Ber. d. ch. G., p. 49.

|| Comptes Rendus, lxxix. 121.

\*\* Ibid., cxxxvi. 94.

¶ Ann. Chem. Pharm., cxxxix. 308.

Van Dorp,\* in 1872, obtained the same result, and proved that the oil  $C_{14}H_{14}$ , which Limpricht had thought was dibenzyl, is benzyltoluol. Finally Zincke,† in 1874, showed that this reaction resembled that of zinc-dust on a mixture of benzylchloride and benzol, and succeeded in isolating a chloride  $C_6H_5CH_2C_6H_4CH_2Cl$  and a complex hydrocarbon. He proved, further, that this synthesis was of little value in determining the constitution of anthracene, since neither anthracene nor benzyltoluol was present in the product of the reaction, but they were formed during distillation by the breaking up of the more complex substances just mentioned.

2. In the year after Limpricht's synthesis was published, Berthelot, in developing his general method for the synthesis of complex hydrocarbons by passing simpler ones through a porcelain tube, heated to redness, obtained anthracene‡ from toluol (confirmed by Graebe§ in 1874), xylol, cumol, and mixtures of benzol with ethylene,|| and of benzol with styrol; also traces of it by heating acetylene to redness in a glass tube over mercury. The same method was applied successfully by Van Dorp¶ to benzyltoluol, that obtained from benzylchloride toluol and zinc-dust, as well as that from benzylchloride and water; by Kramers\*\* to phenol (yellow heat); by Claus and Suckert†† to azobenzol; and by Barbier‡‡ to the mixture of toluol with benzol, and to that of diphenyl with ethylene, although the latter yielded only traces of anthracene. Barbier,‡‡ in 1874, substituted for red-hot porcelain tubes vacuous sealed glass tubes heated to dull redness for a few minutes, and obtained in this way anthracene from benzyltoluol, phenylxylol, diphenylmethan, and liquid ditolyl. While Behr and Van Dorp§§ obtained the same result a year earlier by passing liquid benzyltoluol, or liquid tolylphenylketone over gently heated plumbic oxide. The synthesis from orthotolylphenylketone by the aid of heat has been recently repeated by Ador and Rilliet.||||

3. The next synthesis of anthracene was published in 1872 by Kekulé and Franchimont,¶¶ who obtained a small quantity of anthra-

\* Ber. d. ch. G., '72, p. 1070. Ann. Chem. Pharm., clxix. 207.

† Ber. d. ch. G., '74, p. 276.

‡ Bull. Chem. Soc., vii. 222.

§ Ber. d. ch. G., '74, p. 48.

|| Bull. Chem. Soc., vii. 279.

¶ Ber. d. ch. G., '72, p. 1070. Ann. Chem. Pharm., clxix. 207.

\*\* Ann. Chem. Pharm., clxxxix. 131.

†† Ber. d. ch. G., '75, p. 37.

‡‡ Comptes Rend., lxxix. 121, 660, 810. Also, Ann. Ch. Phys., ser. 5, vii. 515

§§ Ber. d. ch. G., '73, p. 753.

|||| Ibid., '79, p. 2298.

¶¶ Ibid., '72, p. 909.

chinone from the by-products of the distillation of calcic benzoate. Their results were confirmed by Behr\* and Staedel.†

4. Related to this method is that of Barth and Senfhofer,‡ published in 1873, which consists in heating oxybenzoic acid alone, or with sulphuric acid.

5. In 1873, also, anthracene was first obtained by Zincke's reaction; for, although Zincke§ had not succeeded in finding it, Radziszewski and Zaleski|| got it from zinc-dust benzylchloride and benzol, and Paterno and Filetti¶ by the action of zinc-dust on a mixture of benzylchloride and phenol; the latter, however, think that it is not formed directly, but by a secondary reaction from the benzylphenol, and this view is supported by a paper published in the following year by Zincke and Weber,\*\* who obtained it from a mixture of zinc-dust benzylchloride and toluol, but suppose that all the anthracene is formed by the breaking up of complex hydrocarbons during the subsequent distillation, in the same way that it is formed from the product of the action of water on benzylchloride. More interesting, therefore, is the synthesis of Piccard.†† who obtained anthrachinone by the action of zinc-dust on the chloride of phtalic acid and benzol at 220°.

Under this head should come also the recent experiments of Friedel and Crafts,‡‡ who, among their beautiful syntheses with aluminic chloride, made anthrachinone from the same mixture, and finally of Ador and Rilliet,§§ who, in 1879, obtained it from the chloride of orthotoluylic acid and aluminic chloride.

6. Paterno and Filetti,||| in a paper published somewhat later, in 1873, describe the synthesis of anthracene by the distillation of benzylphenol with phosphoric pentoxide.

7. In the same year appeared a paper by Grimm,¶¶ from Baeyer's laboratory, describing the synthesis of chinizarine from phtalic anhydride hydrochinone and sulphuric acid; while in 1874, Baeyer and Caro,\*\*\* found that phtalic anhydride yielded, with phenol, benzol-sulphoacid, anisol, anisic acid, or salicylic acid, either oxyanthrachinone or erythroxyanthrachinone, both of which give alizarine by fusion with potassic hydrate; with pyocatechin, guaiacol, or protoca-

\* Ber. d. ch. G., '72, p. 971.

† Ibid., '73, p. 178.

‡ Ann. Chem. Pharm., clxx. 100.

§ Ber. d. ch. G., '73, p. 137.

|| Ibid., '73, p. 810.

¶ Gazz. Chim., '73, p. 121.

\*\* Ber. d. ch. G., '74, p. 1153.

†† Ber. d. ch. G., '74, p. 1785.

‡‡ Comptes Rendus, lxxxiv. 1450.

§§ Ber. d. ch. G., '79, p. 2298.

||| Gazz. Chim., '73, p. 251.

¶¶ Ber. d. ch. G., '73, p. 506.

\*\*\* Ibid., '74, p. 968.

technic acid, alizarine; with hydrochinone (see Grimm), chinic acid, thiochronic acid, or the  $\alpha$  and  $\beta$  sulphoacids of hydrochinone, chinizarine. Still later, in 1875,\* they added chlorphenol, boiling-point  $218^\circ$ , to the list of substances which form chinizarine, and converted chinizarine into purpurine by oxidation.

In his last paper† on phtaleines and their derivatives, published in 1880, Baeyer shows their close relation to the anthracene group, ordinary phthalidine being dioxyphenylanthranol, while a corresponding compound can be obtained from triphenylmethancarbonic acid.

8. The syntheses of anthrachinone from benzoylbenzoic acid also begin in 1873, when Plascuda and Zincke‡ obtained a little in oxidizing crude benzyltoluol. In the following year Behr and Van Dorp§ made it by oxidizing tolylphenylketone, and somewhat later in the same year converted  $\beta$  benzoylbenzoic acid into anthrachinone|| by heating it with phosphoric pentoxide, a process which ran smoothly and yielded 26% of the theoretical amount, whereas the para-acid, under the same conditions, gave no anthrachinone whatever. The formation of traces of anthrachinone from the distillation of calcic benzoate alone, and of benzoic acid with phosphoric pentoxide, they ascribe to the previous formation of  $\beta$  benzoylbenzoic acid. Liebermann¶ next showed that fuming sulphuric acid produced essentially the same effect as phosphoric pentoxide, converting the  $\beta$  benzoylbenzoic acid into anthrachinone sulphoacid, and suggested that this method might be of technical value in the future. Rotering and Zincke\*\* obtained a similar result by using phosphoric pentachloride, while Thörner and Zincke†† worked out the process further, and showed that chlorine acting on orthotolylphenylketone produced the same effect. Under this head might also be classed the action of hot plumbic oxide on tolylphenylketone already described in Group 2.

9. Closely related to the preceding group is the synthesis depending on the action of zinc-dust on tolylphenylketone, which was studied by Behr and Van Dorp in 1873;‡‡ also in 1874,§§ when they proved that the para-compound gives no anthracene, and more recently by Ador and Rilliet|||

Finally, the occurrence of (10) anthracene among the products of

\* Ber. d. ch. G., '75, p. 152.

† Ann. Chem. Pharm., ccii. 36.

‡ Ber. d. ch. G., '73, p. 906.

§ Ibid., '74, p. 16.

|| Ibid., p. 578.

¶ Ibid., p. 805

\*\* Ber. d. ch. G., '76, p. 631.

†† Ibid., '77, p. 1477.

‡‡ Ibid., '73, p. 753.

§§ Ibid., '74, p. 16.

||| Ibid., '79, p. 2298.

the action of potassic nitrite on benzylchloride,\* and of (11) anthraquinone from the oxidation of isatropic acid † should be mentioned.

*Discovery and Syntheses of Phenanthrene.*

It is highly probable that Fritzsche,‡ in 1867, encountered phenanthrene in studying the higher fractions of coal-tar with his reagent, as he describes a hydrocarbon melting near 100°; this observation was entirely overlooked, however, and we owe the first definite statements about phenanthrene to Fittig,§ who announced its discovery in August, 1872; but his preliminary notice of it was so imperfect that Glaser, who discovered it at about the same time, sent it to Graebe || for investigation as a new hydrocarbon. In 1873 three independent tolerably complete accounts of it appeared almost simultaneously in the *Annalen der Chemie*; these were by Fittig and Ostermayer,¶ by Graebe,\*\* and by Hayduck.††

In Graebe's article the synthesis of phenanthrene by passing stilbene or dibenzyl through a red-hot tube is described, whereas Dreher and Otto,‡‡ who tried the same experiment in 1870, before the discovery of phenanthrene, naturally overlooked it.

In the following year Graebe §§ added toluol to the substances, which form phenanthrene under these conditions; and Barbier ||| announced that Fritzsche's phosene (see page 64) was a mixture of anthracene and phenanthrene, since he succeeded in getting the characteristic test, brown plates, with Fritzsche's reagent (dinitroanthrachinone) from such a mixture. Armed with this test, he then proceeded to examine the anthracenes from various syntheses, and found phenanthrene in those made by the action of heat on styrol and benzol, ethylene and benzol, benzyltoluol, phenylxylo, and diphenylmethane; also in the anthracene made from benzylchloride by heating with water, and in that from natural alizarine by reduction with zinc-dust; as in all these cases the phenanthrene could not be detected by any other test except Fritzsche's reagent, there seems good reason for receiving these results with caution, especially as he himself has proved by direct experiment ¶¶ that anthracene cannot be converted into phe-

\* Brunner, Ber. d. ch. G., '76, p. 1744. ¶ Ann. Chem. Pharm., clxvi. 361.

† Fittig, Ber. d. ch. G., '79, p. 1739.

\*\* Ibid., clxvii. 131.

‡ Zeitschr. fur Chem., '67, p. 293.

†† Ibid., clxvii. 177.

§ Ber. d. ch. G., '72, p. 933.

‡‡ Ibid., cliv. 176.

|| Ibid., p. 968.

§§ Ber. d. ch. G., '74, p. 48.

||| Comptes Rendus, lxxix. 121, 660, 810; Ann. Chim. Phys., ser. 5, vii. 515.

¶¶ Ann. Chim. Phys., ser. 5, vii. 515.

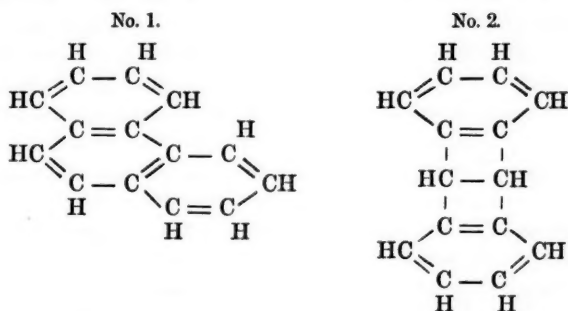


nanthrene by heat. By passing a mixture of ethylene and diphenyl through a red-hot porcelain tube, however, he obtained a large quantity of phenanthrene, and also by heating liquid ditolyl or stilbene to dull redness in a sealed tube. Finally Kramers\* found a trace of phenanthrene among the products from passing phenol through a yellow-hot tube.

*Constitution of Anthracene and Phenanthrene.*

Dumas and Laurent, in their first article on anthracene, considered it a polymerized naphthalene. Anderson, after establishing the formula, called attention to the fact that anthracene and anthrachinone differed from stilbene and benzil only by two atoms of hydrogen in each case. Berthelot, in 1867, on account of its formation from toluol at a red heat, gave it the formula  $C_6H_4[C_6H_4C_2H_2]$ ,† which he showed later in the same year was supported also by Limpricht's synthesis, and his own decompositions of anthracene‡ with hydriodic acid; he considered it an "acetylodiphenylene," but pointed out the fact that, while the calculated boiling-point of this substance should be  $310^\circ-320^\circ$ , the boiling-point of anthracene is in reality  $360^\circ$ .

In 1870, Graebe and Liebermann proposed two formulas for anthracene, giving the preference to No. 1, on the ground of the syntheses



by Limpricht from benzylchloride, and Berthelot from styrol and benzol; also because this formula is like that of naphthalene, which they show is allied to anthracene in many respects; but these arguments were overturned in 1872 by the discovery of phenanthrene,

\* Ann. Chem. Pharm., clxxxix. 132.

† Calculated to modern atomic weights.

‡ Bull. Chem. Soc., ix. 295.

which not only resembled naphthalene more closely than anthracene did, but yielded diphenic acid and other undoubted derivatives of diphenyl, and was therefore entitled to the first formula, leaving the second for anthracene. This arrangement of the formulas was confirmed by Van Dorp's synthesis of anthracene from benzyltoluol, and by some experiments by Graebe,\* which showed that phenanthrene-chinone gave diphenyl on distillation with soda-lime, while anthrachinone gave benzol and a very little diphenyl, indicating that there is no direct union of the rings in the latter.

Finally the syntheses from phthalic acid, and the formation of phthalic acid by oxidation, or the action of sulphuric acid † on anthrachinone, established without doubt the ortho position of the connecting atoms of carbon in one of the benzol-rings of anthracene, which was still further confirmed by the syntheses from liquid benzyltoluol and  $\beta$  benzoylbenzoic acid.

At the end of 1873, therefore, the second formula had been universally adopted as that of anthracene, although the position of the two connecting atoms of carbon in one of the benzol rings had not been determined, and the researches of following years, while confirming the points already established, threw no more light on this subject.‡

With phenanthrene the case is different, as the proof of the ortho position of the two additional atoms of carbon has not been neglected. In 1878 Schmitz § argued that this was probably the constitution from the fact that diphenyleneketone and diphenylcarboxylic acid were completely destroyed by oxidation; while somewhat later in the same year the point was proved by Schultz,|| and by Anschütz and Japp,¶ almost simultaneously. Schultz did this by converting Griess's metadiamidodiphenic \*\* acid (made by the reduction of metanitrobenzoic acid with tin and hydrochloric acid) into diioddiphenic acid, and reducing this to a diphenic acid, which he proved was identical with that from phenanthrene (a proof which he did not make perfectly

\* Ber. d. ch. G., '73, p. 63.

† Weith and Bindschedler, Ber. d. ch. G., '74, p. 1106.

‡ Anschütz (Ber. d. ch. G., '78, p. 1213) made diphenyleneketone by heating anthrachinone with calcic oxide, but proves in the same paper that this reaction cannot be used as an argument in regard to the position of the  $C_2H_2$  group in anthracene.

§ Ann. Chem. Pharm., cxci. 115.

|| Ann. Chem. Pharm., cxvi. 1. Ber. d. ch. G., '78, p. 215.

¶ Ber. d. ch. G., '78, p. 211.

\*\* Ibid., '74, p. 1609.

satisfactory till a later paper,\* in 1879). Anschütz and Japp oxidized the sodic salt of the phenanthrenesulphoacid with potassic permanganate, and obtained phthalic acid as the only product, whereas, if phenanthrene were not a diortho compound, isophthalic or terephthalic acid must also have been formed.

In 1879 Merz and Weith † proposed a new formula for phenanthrene,  $\text{C}_6\text{H}_4 = \overset{\text{H}}{\underset{\text{H}}{\text{C}}} - \overset{\text{H}}{\underset{\text{H}}{\text{C}}} = \text{C}_6\text{H}_4$ , founded on the fact that they obtained invariably perchlorbenzol instead of perchlordiphenyl by the exhaustive action of chlorine upon it; the formation of diphenic acid would then be due to an atomic transformation during the process of oxidation. This hypothesis, however, can hardly be considered as throwing doubt on the constitution of phenanthrene until supported by additional facts, especially since Japp ‡ has shown by the formation and properties of the  $\beta$  phenanthrenecarboxylic acid that the  $\text{C}_2\text{H}_2$  group behaves as if it were part of a benzol ring.

At present, then, the constitution of phenanthrene must be considered as settled, while it still remains to prove the position of the two connecting atoms of carbon on one of the benzol rings in anthracene.

#### *Action of Sodium on Orthobrombenzylbromide.*

In the hope of settling the constitution of anthracene we have studied the action of sodium on orthobrombenzylbromide, since this might lead to the formation of a hydride of anthracene by the union of two molecules, the side-chain of each being joined to the ring of the other, and of phenanthrenedihydride if the two side-chains and the two rings were united. As these two reactions were likely to take place side by side, we expected that our product would consist of a mixture of these two hydrocarbons.

Orthobrombenzylbromide dissolved in anhydrous ether § was warmed with sodium for some days, fresh shavings of sodium, or sodium shot, || being added from time to time, until the bright surfaces were no longer tarnished. The greater part of the sodium was then removed, and,

\* Ber. d. ch. G., '79, p. 235.

† Ibid., p. 677.

‡ Ibid., '80, p. 573.

§ When toluol was used in place of ether, the reaction ran so slowly that even after boiling for several days the sodium was but little affected.

|| The sodium shot was made by melting sodium under toluol, and shaking (Wislicenus, Ann. Chem. Pharm., clxxxvi. 212). It seemed not to be so effective as thin shavings of sodium.

after treatment with dilute alcohol to destroy the remainder, the product of the reaction thoroughly washed with water; the yellowish viscous mass thus obtained was oxidized with chromic anhydride, and upon subliming the product, after removing the portions soluble in water and sodic hydrate, yellow needles were obtained which melted at  $273^{\circ}$ , and gave with zinc-dust and sodic hydrate a red color; they were therefore *anthrachinone*.

0.5745 gr. of the substance gave on combustion 1.7000 grs.  $\text{CO}_2$  and 0.2180 gr.  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{14}\text{H}_8\text{O}_2$ .	Found.
Carbon	80.75	80.67
Hydrogen	3.84	4.21

The anthrachinone was further converted into the bromine compound, which, by fusion with potassic hydrate yielded alizarine.\*

A second portion of the orthobrombenzylbromide treated with sodium, and afterward freed from it in the same way, was distilled with steam for a long time; a white substance passed over solidifying in part in the condenser, which was proved to be dibenzyl by its odor, its melting-point  $52^{\circ}$ , and the following analysis:—

0.2435 gr. of the substance gave on combustion with  $\text{PbCrO}_4$ † 0.8240 gr.  $\text{CO}_2$  and 0.1700 gr.  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{14}\text{H}_{14}$ .	Found.
Carbon	92.31	92.27
Hydrogen	7.69	7.75
	100.00	100.02

No anthracenedihydride could be found in the distillate with steam, although it was carefully searched for.

The residue left in the flask, after the distillation with steam, was a yellow viscous mass, which can be most conveniently purified after distillation *per se*, as this destroys the greater part of the viscous substances containing bromine, which render the extraction with a solvent toilsome and unsatisfactory. The distillate, which passed over without a pause from  $260^{\circ}$  to redness, consisted of a solid mixed with oil, and had a very disagreeable rank smell, different from that of the

\* A preliminary notice of the work up to this point was published, Ber. d. ch. G., '79, p. 1965.

† Owing to the ease with which the substance sublimes, great difficulty was encountered in getting a satisfactory combustion.

undistilled substance. The less volatile parts of the distillate were easily converted by washing with alcohol and ether into white plates with a blue fluorescence, which melted at  $212^{\circ}$ , and were therefore *anthracene*. The residue left by evaporation of the alcoholic washings consisted of dibenzyl, a brown viscous substance containing bromine, and a small amount of a yellow oil: it was tested for phenanthrene by oxidation with chromic anhydride in glacial acetic acid solution, and treatment of the product, after it had been freed from chromic compounds with water, and from acids by weak sodic hydrate, with warm acid sodic sulphite; the solution thus formed was filtered, acidified with hydrochloric (better nitric) acid, and allowed to stand for some time, when it deposited a yellow precipitate, which melted at  $198^{\circ}$ , and was therefore *phenanthrenechinone*. For further confirmation it was tested, according to Laubenheimer,\* as follows: a little of the substance was dissolved in about 5 cc. of glacial acetic acid, a few drops of toluol, and 8-10 drops of sulphuric acid were added, and the mixture allowed to stand over night. It was then poured into water, which, shaken with ether, imparted to it a deep claret-red color, exactly like that obtained from pure phenanthrenechinone under the same conditions.

In a third experiment 20 grammes of orthobrombenzylbromide were treated with sodium for nearly a month in the way already described, but, instead of adding water at once to the product, the organic matter was extracted from the sodium and sodic bromide as far as possible with ether and benzol, in order to avoid the reducing action of the hydrogen set free by water. The residue insoluble in these solvents was finally treated with water, and the small amount of organic matter thus obtained added to that at first extracted. The amount of dibenzyl in this product was notably smaller than in those which had been treated directly with water. In a weighed portion an attempt was made to determine the amount of phenanthrene, by adding picric acid to a strong alcoholic solution, but no crystals of the picric acid compound of phenanthrene separated; the solution was therefore evaporated, and in this way a few red crystals were obtained, which had the form of the compound of anthracene with picric acid, and melted in the crude state near  $168^{\circ}$  instead of at  $170^{\circ}$ ; the quantity was too small to admit of purification. The formation of the anthracene compound, which is decomposed by alcohol, apparently from an alcoholic solution, can be explained by the supposition that it was not formed

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\* Ber. d. ch. G., '75, p. 224.

until the alcohol had evaporated, leaving the anthracene and picric acid dissolved in the oily impurities. In point of fact, it was obtained by imitating the above conditions; that is, evaporating an alcoholic solution of anthracene and picric acid, to which a few drops of toluol had been added. The experiment would seem to show that phenanthrene as such does not exist in the original product.

To meet the objection, which might be urged, that the anthracene obtained in the second experiment was not formed directly by the action of sodium on the orthobrombenzylbromide, but during the distillation of the viscous mass, which resembled the substance obtained by Zincke both from his reaction and the action of water at high temperatures on benzylchloride, another portion was treated with ether and hot alcohol, which removed a yellow oil and left *anthracene* identified by crystallizing in white plates melting at  $210^{\circ}$ . The yellow oil contained either phenanthrene or its dihydride,\* as it gave phenanthrenequinone by oxidation, but we were unable to determine which of these substances was present on account of the small amount at our disposal. We are therefore in doubt as to the way in which the phenanthrene occurs in our product; for, on the one hand, we could not obtain the picric acid compound either from the original product or the yellow oil, while, on the other, a substance crystallizing in plates melting between  $170^{\circ}$  and  $190^{\circ}$ , which has appeared more than once in the course of this work as an intermediate product in the purification of the anthracene, yields on oxidation anthraquinone and phenanthrenequinone, and seems therefore to be a mixture of the two free hydrocarbons.

No anthracenedihydride could be found in any of the products, nor have we succeeded in detecting benzyltoluol or ditolyl, although it is highly probable that they were formed in addition to the dibenzyl; but the acids resulting from the oxidation appeared in such small quantities, and so contaminated with a brown impurity formed from the viscous brominated substance, that it was impossible to obtain any definite result from them. The viscous substances, too, containing bromine, which were the principal products of the reaction, have resisted thus far all our efforts to bring them into a form suitable for analysis, but we hope to return to this part of the subject hereafter.

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\* Phenanthrenedihydride has never been prepared with certainty, although Barbier (Comptes Rendus, lxxix. 121) thought it was formed by the reduction of phenanthrene with sodium amalgam.

Finally the following quantitative results were obtained:—

Organic product from 20 grs. orthobrombenzylbromide	10.85 gra.
Calculated product if free from bromine . . . . .	7.12 “
Bromine not removed by the sodium . . . . .	3.73 “
Bromine in 20 grs. orthobrombenzylbromide . . . . .	12.88 “
Bromine removed as bromide of sodium . . . . .	9.71 “
Bromine not removed by the sodium . . . . .	3.17 “

The “bromine removed as bromide of sodium” was determined by precipitating 7.727 grs. of the wash-water with argentic nitrate, which gave 1.482 grs. of argentic bromide. As the weight of the wash-water was 119 grs., this corresponds to the result given above. The two determinations of the amount of bromine not removed by the sodium agree as closely as could be expected when the losses resulting from the repeated extraction and washing of the viscous organic products are taken into account.

75.4 per cent of the whole amount of bromine contained in the orthobrombenzylbromide was therefore removed by the sodium.

*Determination of the Amount of Anthracene by Luck's\* Method.*—1.04 grs. of the product, oxidized, first with chromic anhydride dissolved in glacial acetic acid, and afterward with an alkaline solution of potassic permanganate, gave 0.158 gr. of anthrachinone, corresponding to 0.135 gr. of anthracene, that is, 1.409 grs. from the 20 grs. of orthobrombenzylbromide used, or 19.78 per cent of the theoretical yield.

*Determination of the Amount of Phenanthrene.*—2.44 grs. of the original product, oxidized carefully by adding a strong aqueous solution of chromic anhydride to a hot solution of the substance in glacial acetic acid as long as a drop of the oxidizing agent made the liquid boil,† on extraction of the product with acid sodic sulphite and acidification with nitric acid, yielded 0.05 gr. of phenanthrenequinone, which corresponds to 0.0428 gr. of phenanthrene; that is, from 20 grs. of orthobrombenzylbromide 0.190 gr., or 2.66 per cent of the theory. The amount of phenanthrene actually formed must have been somewhat larger than this, as some of the chinone was undoubtedly destroyed by the chromic anhydride,—in fact, the operation can hardly be called a quantitative one.

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\* Zeitschr Anal. Chem., '73, p. 347; '74, p. 251.

† Liebermann and Hörmann, Ber. d. ch. G., '79, p. 591.



From the work described above, it appears that 20 grs. of ortho brombenzylbromide yielded, —

Total organic product . . . . .	10.850 grs.
Anthracene . . . . .	1.409 "
	<hr/>
	9.441 "
Phenanthrene . . . . .	0.190 "
	<hr/>
	9.251 "
Dibromdibenzyl, or its isomeres, calculated from 3.17 grs. of unremoved bromine . . . . .	6.738 "
	<hr/>
Undetermined, containing phenanthrene, dibenzyl, benzyltoluol, and ditolyl . . . . .	2.513 "

#### *Summary of Results.*

Orthobrombenzylbromide when treated with sodium yields anthracene (identified by its melting-point  $212^{\circ}$ , the formation of anthrachinone melting-point  $273^{\circ}$ , and of alizarine; 19.78% of the theoretical yield); and phenanthrene (identified by the melting-point of its chinone  $198^{\circ}$ , and by Laubenheimer's test; 2.66% of the theoretical yield). Certainly part, and probably all, of the anthracene occurs in the free state; no anthracenedihydride could be found. Our experiments leave us in doubt as to the way in which the phenanthrene occurs. Dibenzyl was also obtained, an oil possibly benzyltoluol or ditolyl, and a viscous substance containing bromine.

By this synthesis of *anthracene* from orthobrombenzylbromide, it is proved that the *two connecting carbon atoms are attached to each ring in the ortho position*, and thus the last doubt about the constitution of anthracene is removed.

The synthesis of phenanthrene, while it confirms the ortho attachment of the two additional atoms of carbon, proves nothing either for or against the formula recently proposed by Merz and Weith.

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The publication of the preliminary notice of this work, already mentioned, drew out an article from Von Pechmann,\* describing work done at about the same time as ours, in which he applies to anthracene the ingenious method contrived by Graebe for determining the

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\* Ber. d. ch. G., '79, p. 2124.



constitution of naphthaline as follows: bromorthobenzoylbenzoic acid, prepared by the action of bromphtalic acid on benzol in presence of aluminic chloride, was converted into bromanthrachinone by heating with sulphuric acid, which on fusion with potassic hydrate gave erythoxyanthrachinone, and, as this when oxidized yielded phtalic acid, the conclusion drawn from our experiments that anthracene is a diortho substance is confirmed by his work.

## V.

## CONTRIBUTIONS TO NORTH AMERICAN BOTANY.

BY ASA GRAY.

Presented June 9, 1880.

I. *Notes on some Compositæ.*

As the portion of the Synoptical Flora of North America which contains this order, now under elaboration, cannot immediately be published, it will be advantageous to fix some of the results already reached by a few notes and characters.

**VERNONIA.** The North American species, although few, are difficult, both on account of variation and probable hybridization. The principal change from Torrey and Gray's Flora now made is the restoration of *V. altissima*, Nutt., standing between *V. fasciculata* (to which some of it had been referred) and *V. Baldwinii* or *V. Novboracensis*. A good new species comes in under the name of

**VERNONIA LETTERMANNI**, Engelm. in litt. *V. Jamesii* et *V. fasciculatæ* affinis, glaberrima, lævis; foliis angustissime linearibus eveniis integerrimis planis; capitulis numerosis paniculato-cymosis pedunculatis lanatis cylindraceis 10-14-floris (sempollicaribus); involucri bracteis acutis vel acuminatis adpressis inappendiculatis, externis ovato-subulatis, intimis angusto-lanceolatis purpureis; acheniis secus costas parum scabris. — Arkansas, on Cooper's Creek, Dr. J. M. Bigelow, and on sand-bars of the Washita, Lettermann.

**AGERATUM LITTORALE** is the name adopted for the *Cælestina maritima* of Torr. & Gray, Fl. ii. 64, which is not *Ageratum maritimum*, HBK., that being a true *Ageratum* with diminutive pappus. A species of the Florida coast is likely to occur on shores of the Gulf and West Indies; but this has not yet been identified elsewhere.

**EUPATORIUM AMBIGUUM**, Hook. This name comes up in place of *E. parviflorum*, Ell., non Swartz. **E. BETONICUM** and **E. DISSECTUM** are *Conoclinium betonicum*, DC. (of which var. *subintegrum* is probably *E. Hartwegi*, Benth.), and *C. dissectum*, Gray, Pl. Wright.

BRICKELLIA SQUAMULOSA, Gray, Proc. Am. Acad., xv. 30, comes into our flora, being found by Mr. Greene to occur abundantly in New Mexico. It is woody only at the base, sending up long and simple stems which bear narrowly linear leaves, 2 or 3 inches long and less than two lines wide the first year; they flower the next year, when they bear only squamiform and minute leaves or bracts.

GARBERIA FRUTICOSA, Gray, in Proc. Acad. Philad., Nov. 1879, 379. Having followed Bentham and Hooker in the restoration of Cassini's genus *Trilisia*, I found Nuttall's *Liatris fruticosa* still more worthy of generic distinction. But, in taking up Nuttall's subgeneric name of *Leptoclinium* (in Proc. Am. Acad. xv. 48) I overlooked the patent fact that Gardner had used that name, somewhat illegitimately, for an allied Brazilian genus. Whereupon, as the above reference shows, I promptly took the opportunity of dedicating our genus, to the rediscoverer of the plant, Dr. A. P. Garber, of Columbia, Pennsylvania, a most devoted and acute botanist, who has done more for the development of the botany of subtropical Florida of late than any one, except Mr. A. H. Curtiss, who is still in the field.

APLOPAPPUS. The primary sections of this extended genus, as here accepted, are *Prionopsis*, *Aplopappus* proper (which is made to include *Eriocarpum*, Nutt., *Pyrrocoma*, Hook., *Homopappus*, Nutt., and *Sideranthus*, Nutt.), *Isopappus*, *Stenotus*, *Ericameria*, and *Macronema*.

APLOPAPPUS INTEGRIFOLIUS, T. C. Porter, is taken up from an unpublished name of a plant collected in Wyoming by J. M. Coulter and also by Burke, a species between *A. lanceolatus* or *paniculatus* and *A. uniflorus*. *A. Parryi*, which inclines on the one hand toward *Solidago*, especially in a reduced form (var. *depauperatus*), is included in the *Stenotus* section. *A. nanus* takes in *A. cervinus* of Watson as a variety, and the following new species are brought together into a subsection of the *Ericameria* section, which is transitional between that and the section *Macronema*.

APLOPAPPUS WATSONI. Viscidulo-pubescent, spithamæus; ramis fastigiatis subherbaceis e basi lignosa; foliis lanceolatis seu angustospathulatis oblongisve mucronato-acuminulatis membranaceis (vix pollicem longis); capitulis pauciusculis subglomeratis; bracteis involucri lanceolato-linearibus acutis vel acuminatis plerisque tenuiter chartaceis vel paucis herbaceis, omnibus erectis; ligulis 4-8; floribus disci vix numerosioribus; appendicibus styli ramorum setaceo-filiformibus. *Aplopappus suffruticosus*, Eaton, Bot. King, 159, pro parte. — Northern Nevada, Watson, Palmer, &c.

**APLOPAPPUS GREENEL.** Suffruticosus, pedalis, tenuiter viscoso-puberulus, ceterum glaber; caulibus usque ad capitulum subsolitarium foliosis; foliis spathulato-oblongis parvulis (lin. 6-10 longis 2-3 latis); involucri subglandulosi bracteis angusto-lanceolatis acutis superne vel apice tantum foliaceis et patentibus; ligulis 3-7; fl. disci 13-16; styli ramis *Macronemæ*. — N. California, on the Scott Mountains of Siskiyou Co., E. L. Greene. Mountains of Union Co., Oregon, Cusick.

**APLOPAPPUS MOLLIS.** Præcedenti affinis, pube molli incana tomentosus; involucri bracteis (intimis linearibus scariosis exceptis) oblongis vel brevi-lanceolatis mucronatis, apice erecto foliaceo; ligulis 3-5. — High mountains of Union Co., Oregon, with the preceding. Cusick.

**SOLIDAGO** is divided into three primary sections or subgenera, viz. *Virgaurea*, *Euthamia*, and *Chrysoma*. The *Chrysastrum* section of Torrey and Gray is reduced to a subsection of the first, and is made to include *S. petiolaris*.

**S. BIGELOVII** is a New Mexican species founded on *S. petiolaris*, var., Gray in Bot. Mex. Bound. 79, collected by Bigelow, Wright, and Parry, and placed next to *S. Lindheimeriana* of Scheele, which was in Pl. Lindh. referred to *S. speciosa*, var. *rigidiuscula*.

**S. SPATHULATA**, DC. is the *S. spiciformis*, Torr. & Gray, an older and better name.

**S. SPECTABILIS** is the *S. Guiradonis* var. *spectabilis* of Eaton in Bot. King; but it and its relatives are of uncertain limitation.

**S. CHAPMANII.** *S. odoræ* proxima, validior, rigidior; caule superne scabro-puberulo; foliis brevibus oblongis vel ellipticis apice obtuso vel rotundato, summis rotundatis. — Pine barrens of Florida, Chapman (*S. odora* of his Flora, in part), Dr. Garber.

**S. WRIGHTII.** *Corymbosæ*? cinereo-puberula, scabrida; foliis caulinis oblongis seu lanceolato-ellipticis acutiusculis integerrimis rigidiusculis haud triplinerviis (radicalibus ignotis); capitulis subcorymboso-glomeratis; involucri bracteis lanceolatis acutiusculis, extimis puberulis; floribus radii 6-8, disci plus 20; acheniis pubescentibus. *S. petiolaris*, var., Gray Pl. Wright. i. 94. *S. Californica*, var., Rothrock, in Wheeler Rep. vi. 145. — W. Texas to Arizona, Wright, Bigelow, Rothrock.

**APHANOSTEPHUS**, DC. This genus, first brought into its present shape in *Plantæ Wrightianæ*, i. 93, has now five recognized species, which are arranged and characterized thus: —

\* Pappus brevissime coroniformis, margine primum ciliolato-fimbriato cæterum integro; corollæ disci tubus parum incrassatus.

A. ARIZONIGUS. Puberulus, subintegrifolius; pedunculis apice clavatis; ligulis brevibus; acheniis angustis teretibus costis circiter 10 angustis striatis. *A. ramosissimus*, Rothrock in Wheeler Rep. vi. 147. — Arizona, on the Gila, Rothrock.

A. RAMOSISSIMUS, DC. Hispidulo-pubescent; foliis inferioribus sæpe laciniatis vel pinnatifido-incisis; pedunculis gracilibus; ligulis longioribus; acheniis parum pauci-costatis. — Texas and adjacent Mexico.

A. HUMILIS, Gray. Diffusus, pube molli cinereus; foliis sæpius dentatis vel pinnatifidis; pedunculis gracilibus; acheniis brevioribus costato-angulatis. — S. W. Texas and Mexico.

A. RAMOSUS. Præcedenti affinis, parum pubescens; foliis omnibus linearibus integerrimis. *Keerlia ramosa*, DC. Prodr. v. 310. — Mexico, Keerl.

\* \* Pappus conspicuus, e corona dentata vel laciniata; corolla tubo basi demum incrassato indurato diu persistente in achenio valde angulato-costato. *Leucopsidium* et *Keerlia skirrobasis*, DC.

A. ARKANSANUS, Gray. — Plains of Arkansas and Texas.

Var. HALLII. Minor; foliis imis sæpius pinnatipartitis; corona pappi profundius 4-5-lobata, lobis subulato-acuminatis! — Hempstead and Austin, Texas, E. Hall, no. 303, 304.

A proposed new genus of the group to which *Aphanostephus* and *Keerlia* belong is

GREENELLA, Nov. Gen. *Comp-Asteroidearum*. Capitulum heterogamum, radiatum, multiflorum; fl. radii 12-16 fœmineis, disci hermaphroditis, omnibus fertilibus. Receptaculum convexiusculum, nudum, parum alveolatum, alveolis dentatis. Involucrum latum; bracteis imbricatis pauciseriatis oblongis coriaceis margine (saltem interiorum) scariosis, apice obtuso, dorso viridi-herbaceo, exterioribus brevioribus. Ligulæ oblongæ exsertæ. Corollæ disci tubuloso-infundibuliformes, tubo proprio brevi, limbo 5-lobo. Antheræ inclusæ. Styli rami fl. herm. longe exserti, appendicibus linearibus complanatis obtusiusculis hirtello-puberis parte stigmatifera quadrata 4-plo longioribus instructi. Achenia oblongo-turbinata, canescenti-puberula, 8-costata, basi apiceque truncata, pappo brevi coroniformi multisetuloso-dissecto superata. — Herba parvula, Arizonica, e radice ut videtur bienni vel perenni ramosa, diffusa fere glaberrima; foliis alternis integerrimis parvis, imis lanceolatis hispidulo-ciliolatis, superioribus linearibus decrescentibus

margine lævibus; capitulis ramulos nudos terminantibus; ligulis albis majusculis; corollis disci forte albidis.

GREENELLA ARIZONICA. Near Tucson, S. Arizona, Rev. Edward Lee Greene (an enterprising botanist and most acute observer, to whom the genus is dedicated, and who discovered the plant in the year 1877); also J. G. Lemmon, who collected it in a more advanced state in the spring of 1880. If the ray-flowers of this plant were yellow instead of white, it would be referred to the genus *Xanthocephalum*, and the habit is nearly that of *X. linearifolium* and *X. sericocarpum*. But it shows no trace of the glutinosity or balsamic exudation which so largely prevails in the homochromous *Asteroideæ*. And *Xanthocephalum* has not the peculiar, large and long, much exserted style-appendages which are characteristic of the present plant.

CHÆTOPAPPA, DC. — *Chaetopappa* et *Distasis*, DC.; Benth. & Hook. Gen. ii. 268. The species are

C. ASTEROIDES, DC. — Arkansas and Missouri to the borders of Mexico.

Var. IMBERBIS. Aristis pappi plane nullis; paleis latio-ribus quantoque coroniformi-concretis. — E. Texas, C. Wright.

C. PARRYI. Major, rigidior, hispidula, nunc glabrata; involu- cro turbinato; ligulis 6-7; appendicibus styli fl. disci brevibus obtusissimis; acheniis glaberrimis, fertilibus fusiformibus subcompressis 4-nervatis; pappi fl. radii paleis firmioribus cuneiformi-quadratis apice truncato laciniato-fimbriatis, aristis aut nullis aut 1-3 tenellis; acheniis disci plerisque inanis haud aristatis. *Distasis modesta*, Gray in Bot. Mex. Bound. 78. — Mt. Carmel on the Rio Grande, Parry.

C. MODESTA. Involu- cro late campanulato, bracteis pluribus obtusi oribus; ligulis 9-20; fl. disci 40-60 plerisque fertilibus; appendicibus styli angustioribus acutiusculis; acheniis magis compressis; pappi paleis 5 oblongis eroso-truncatis aristis sat validis alternantibus. *Distasis modesta*, DC. Prodr. v. 279. — Texas and adjacent Mexico.

An anomalous *Asteroideous* Composita was collected on the adobe plains of S. W. Colorado by Mr. Brandegee, of which additional speci- mens are desired. It has the general aspect of some of the pauci- radiate *Erigerons*, such as *Erigeron Bigelovii*; and the characters are of that genus, except that the simple pappus consists of irregular awn-bearing paleæ.

TOWNSENDIA, Hook. Ever since the discovery of a consider- able number of species, this very characteristic genus of the Rocky

Mountain region has been particularly difficult. The result of a recent study of it, in the form of the following synopsis of the species, may assist our botanists.

- \* Involucri bracteæ insigniter sensim acuminatæ: capitulum amplum.
- + Annuæ vel biennes, caulescentes, pube hirsutula decidua demum glabrata: bracteæ involucri lato- seu ovato-lanceolatae, marginibus plerumque latissime albido-scariosis: ligulæ læte violaceæ vel cæruleæ.
- ++ Pappus abbreviatus, persistens, corneus, ex aristis 2 subulatis et squamellis demum rigidis sæpius coroniformi-concretis: achenium lato-obovatum glabratum: involucrum fere *T. grandifloræ*.

T. EXIMIA, Gray, Pl. Fendl. 70. — Northern New Mexico and Colorado, Fendler, Bigelow, &c.

- ++ ++ Pappus saltem disci plurisetosus generis: achenium angustobovatum.

T. GRANDIFLORA, Nutt. Mox decumbenti-patens, angustifolia; involucri bracteis acumine cuspidato; pilis achenii sub lente glochidiato-capitellatis: pappus radii e squamellis brevibus. — Wyoming and Nebraska to New Mexico.

T. PARRYI, Eaton in Am. Nat. viii. 212. Erectus, nanus, simplex; foliis spathulatis: involucri latissimi bracteis angustioribus tenuioribus minus attenuatis, extimis parum acuminatis; acheniis canescenti-pubescentibus, pilis apice acutis vel 1-2-dentatis; pappo radii ut disci plurisetoso. — Rocky Mountains of Wyoming and E. Idaho, Hayden, Parry.

Var. ALPINA. Forma depressa, cinereo-pubescent, parvifolia; caule florifero abbreviato vel fere nullo; bracteis minus acuminatis; ligulis "roseo-purpureis." — High divide between Stinking Water and the Yellowstone (confounded with *T. spathulata*), Parry.

- + + Perennis e caudice stoloniformi, depressa, pilis longis arachnoideis lanosissima; capitulo intra folia rosulata spathulato-obovata sessili: bracteæ involucri lineares, molles: pappus disci et radii plurisetosus, tenuis.

T. CONDENSATA, Parry in Am. Nat. viii. 213 (char. ex D. C. Eaton). — Wyoming, on an alpine peak of the Owl Creek range, T. D. Putnam.

- \* \* Involucri bracteæ parum vel haud acuminatæ: capitulum minus vel angustius.

+ Pili achenii gracilia, copiosa, simplicissima, nonnulla apice 2-3-fida, lobis vel denticulis parum patentibus acutis vel acutiusculis: capitula mediocria, involucri minus imbricato, pedunculo sæpius nudo: ligulæ roseo-purpureæ, rarius albæ: annuæ vel biennes, occidentales.

++ Pappus radii plurisetosus disci conformis vel brevior.

T. FLORIFER. Spithamæa, cinereo-hirsuta; caulibus e radice annua gracilibus; foliis linearibus imisve subspathulatis acutis nunc apiculato-acuminatis; involucri bracteis lineari-lanceolatis parum inæqualibus. *T. strigosa*, Gray in Wilkes Exped. xvii. 344, non Nutt. *Erigeron florifer*, Hook. Fl. Bor.-Am. ii. 20. *Aplopappus florifer*, Hook. & Arn. Bot. Beech. 351. *Stenotus florifer*, Torr. & Gray, Fl. ii. 238. — Sandy banks of the Columbia River and its tributaries (as far north as Wenass Valley, Lyall), and in the dry region east of the Cascades.

T. SCAPIGERA, Eaton. Humilior, hirsuto-pubescent; caulibus scapiformibus (inferne 1-2-foliatis); foliis radicalibus spathulatis, lamina sæpius lata brevi; involucri bracteis latiuscule lanceolatis. Bot. King, 145, t. 17. *Aplopappus florifer*, var. Hook. & Arn. l. c. ? — Mountains of N. Nevada and N. E. California, Watson, Lemmon, Mrs. Austin.

Var. CAULESCENS, Eaton, l. c., is a summer form, becoming sparingly leafy-stemmed, slender, and with rather smaller heads. — Monitor Valley, Nevada, Watson.

Var. AMBIGUA is still more leafy-stemmed, with white rays, and the pappus in the ray shorter than that of the disk. — Rabbit Valley, Utah, Ward.

++ ++ Pappus radii setoso-squamellatus latitudine achenii brevior.

T. WATSONI. Pube brevi adpressa subcinerea: caulibus e radice gracili patentibus sæpe ramosis parceque foliatis; foliis anguste spathulatis; capitulis sat numerosis brevi-pedunculatis; bracteis involucri oblongo-lanceolatis; pilis achenii brevibus obtusis vel apice dentibus 2-3 obtusis instructis. *T. strigosa*, Eaton, l. c., non Nutt. — Utah, on the shore of Stanbury Island, Great Salt Lake, Watson.

+ + Pili achenii aut omnes aut plurimi glochidiato-capitellati, i. e. apice breviter bidentati, dentibus obtusis recurvis subglandulosis?

++ Capitulum sat magnum ( $\frac{3}{4}$ -pollicare); involucri pluriseriatim imbricato: plantæ fere glabræ, depresso-acaulescentes e radici perenni: folia plana, inferne longe attenuata, coriacea, capitulum longe superantes.

T. WILCOXIANA, Wood. Foliis lineari-spathulatis (1-3-pollicaribus);



capitulo sæpius unico subpedunculato; involucri bracteis lanceolatis, intimis linearibus acutiusculis; pappo radio et disci conformi e setis gracillimis elongatis. Bull. Torr. Club, vi. 163, & Bot. Gazette, iii. 50. — Colorado and Indian Territory, E. K. Smith, Dr. Wilcox, and Arizona, Lemmon.

T. ROTHROCKII, Gray. Foliis lato-spathulatis brevibus circa capitulum sessile rosulato-confertis; involucri brevioris latiore, bracteis oblongis plerumque obtusis; pappus radii e setulis squamellatis latitudinem achenii haud excedentibus, nunc 1 vel 2 longioribus. Rothrock in Wheeler Rep. vi. 148, t. 7. — Alpine region of the mountains around South Park, Colorado, Rothrock.

++ ++ Capitula majuscula ( $\frac{2}{3}$ – $\frac{1}{2}$ -pollicaria), plerumque sessilia; involucri pluriseriatim imbricato: pappus radii sæpius plurisetosus: plantæ sericeo- vel striguloso-pubescentes, radice perenni, *T. incana* forte excepta.

T. SERICEA, Hook. Depresso-acaulescens, demum multiceps et pulviniformis; foliis linearibus seu lineari-spathulatis circa capitulum (pollicare vel minus) arcte sessile confertis eumque æquantibus vel superantibus; bracteis involucri angusto-lanceolatis plerisque acutis; ligulis albis vel purpureo tinctis; pappo sæpius conformi plurisetoso (forma PAPPOSA, Gray, Pl. Fendl. 69), vel radii pauci-setoso, vel brevioris validiore, vel squamellato latitudinem achenii parum excedente. Fl. Bor.-Am. ii. 16, t. 119; Mehan, Flowers, ser. 2, i. t. 47. *Aster ? exscapus*, Richards. — Saskatchewan and Rocky Mountains, lat. 54°, to New Mexico and Arizona; fl. April and May. Very variable in breadth of leaves, size of heads, &c.; commonly with pappus of ray and disk nearly alike, only at the North found with the ray-pappus reduced, either to a few unequal aristiform bristles, as figured by Hooker, or to a circle of setiform squamellæ. In one form the heads are only half an inch long.

Var. LEPTOTES (an spec.?): forma ambigua; capitulis vix semipollicaribus, primario sessili, sequentibus subpedunculatis; foliis angustis. — Middle Park, Colorado, Parry.

T. ARIZONICA. Depresso-subcaulescens, multicipiti-ramosa, 2–3-pollicaris, pube minuta sericeo-canescens; foliis spathulatis brevibus (semipollicaribus) capitulum parum sessile hemisphericum (semipollicare) fulcrantibus vix superantibus; bracteis involucri lanceolatis plerumque obtusis; pappo radio et disci conformi e setis rigidiusculis achenio (lin. 2–3 longo) æquilongis. — Arizona, at Fort Trumbull, &c., Palmer.

**T. INCANA**, Nutt. Depresso-caulescens vel subcaulescens e radice forte monocarpico; caulibus demum  $1\frac{1}{2}$ –4-pollicaribus ramosis; foliis striguloso-cinereis vel canescentibus angusto-spathulatis linearibusque, summis capitulum sessile (semipollicare) fulcrantibus vix superantibus; involucri bracteis sericeis parum obtusis; pappo radii eo disci subdimidio brevior. Trans. Am. Phil. Soc. l. c. *T. Fremontii*, Torr. & Gray in Jour. Bost. Soc. Nat. Hist. v. 108. — Rocky Mountains of Wyoming to Utah and Nevada.

++ ++ ++ Capitula minora ( $\frac{1}{3}$ -pollicaria) inter folia rosulata sessilia: herba depresso-multiceps e radice perenni gracili, villosa-lanata: folia spathulata, conferta: pappus radii et disci conformis e setis gracilibus conjunctim deciduis.

**T. SPATHULATA**, Nutt, l. c. — Rocky Mountains in Wyoming, Nuttall, Parry.

++ ++ ++ ++ Capitula parvula ( $\frac{1}{4}$ -pollicaria), hemisphærica, sæpius brevi-pedunculata: involucrum e bracteis pauciseriatis lato-lanceolatis parum acutis: herbæ caulescentes demum ramosæ, æstivales.

= Glabrata, virides, perennes.

**T. GLABELLA**. Subsimplex, pollicaris vel bipollicaris e rhizomate gracili; foliis crassiusculis spathulatis petioli gracili, summis pedunculo paullo brevioribus; involucrio glabro; pappo plurisetoso conformi sed radii dimidio brevior, vel diverso in radio brevi-squamellato. — La Pagosa, S.W. Colorado, Newberry.

= = Pube tenui strigulosa cinereæ: herbæ primum exiles simplices, demum laxè ramosæ 4–10-pollicares: pappus radii semper brevis, coroniformi-squamellatus, setis 1–2 brevibus raro additis. — § *Nanodia*, Nutt, l. c. (Species nimis affines.)

**T. FENDLERI**, Gray, Pl. Fendl. 70. Radice gracili ut videtur perenni; foliis linearibus; involucri bracteis inæqualibus triserialibus acutis. — Gravelly hills of New Mexico and S. Colorado.

**T. STRIGOSA**, Nutt. l. c. Radice monocarpico gracili; foliis primariis spathulatis, sequentibus linearibus; capitulis parum minoribus, involucri bracteis latioribus acutiusculis tantum biserialibus, exterioribus brevioribus. — Gravelly hills and plains, Wyoming to New Mexico and Arizona.

**T. MEXICANA**, Gray, Pl. Fendl. 70, parum differt involucri bracteis æquilongis obtusissimis. — Saltillo, &c., Mexico, Gregg, Parry.

**ERIGERON**. This genus shades off into *Aster* in more than one direction; and its subgenus *Cænotus* fairly runs into *Conyza*. It can

be limited only by taking into account a combination of characters, and insisting here upon one, there upon another. The general differences between it and *Aster* are found, — 1. in the simpler involucre, of equal neither foliaceous nor appendiculate narrow bracts; 2. in the very numerous and narrow rays of the typical species; 3. in the very short, broad, and obtuse style-appendages; 4. simpler stems, naked above or with few more pedunculate heads; 5. less copious and more fragile pappus; 6. smaller achenia; their nervation is of little importance, but mostly there are only the marginal nerves. We adopt the genus with the extension which Bentham and Hooker, following our lead, now give to it. The various nominal genera which have been predicated on the pappus and the number of ray-flowers are nearly unavailable for good subgenera. The following arrangement, in which the needs of the student are much considered, commences with some of the most Asteroid forms, and ends with the species which merge in *Conyza*. The three primary sections here adopted are not very strictly characterizable; the two larger are connected by a small intermediate group.

§ 1. EUERIGERON. Flores fœminei omnibus ligulatæ ligulis elongatis, in perpaucis nulli.

#### Series 1. Perennes.

1. Species Am.-Bor.-Orientales, glabratae, parvifloræ; ligulis 20–25 plerumque albis; acheniis 2–4-nervatis; pappo simplicissimo. — § *Erigeridium*, Torr. & Gray.

E. HYSSOPIFOLIUS, Michx. Fl. ii. 123. *Aster graminifolius*, Pursh. Fl. ii. 545. — Northern New England to Hudson's Bay, &c., west to shore of Lake Superior.

E. NUDICAULIS, Michx. l. c. *E. vernus*, Torr. & Gray, Fl. ii. 176. *E. integrifolius*, Bertol. Misc. vi. t. 3, non Bigel. *Aster vernus*, L. *Stenactis verna*, Nees, DC. — Pine barrens near the coast, Virginia to Louisiana.

2. Species Californicæ, etc., ligulis nullis; pappo simplici.

\* Subcaulescens, pedunculis scapiformibus monocephalis.

E. BLOOMERI, Gray, Proc. Am. Acad. vi. 40. — Sierra Nevada, California to W. Oregon.

\* \* Foliosissimæ, humiles; capitulis sæpius solitariis.

E. SUPPLEX, Gray, Proc. Am. Acad. vii. 353. — N. E. California, Bolander, &c.

E. MISER, Gray, Proc. Am. Acad. xiii. 372. — Sierra Nevada near Summit.

\* \* \* Foliosissimæ, elatiores glabræ; capitulis subcymosis.

E. INORNATUS. *E. foliosus*, var. *inornatus*, Gray, Bot. Calif. i. 330. — California to Washington Terr.

3. Species occidentales; caulibus sæpe ramosis foliatis e rhizomatibus vel caudice gracilibus; capitulis parvulis, involuero magis imbricato (bracteis 2-3-seriatis, exterioribus brevioribus); ligulis 12-40; acheniis binerviis (exterioribus nunc 3-nerviis); foliis viridibus nec canescentibus.

\* Californicæ; caulibus erectis inferne simplicibus apice subcymosoramosis; pappo simplici.

E. FOLIOSUS, Nutt.; Gray, Bot. Calif. i. 329. *E. Douglasii*, Torr. & Gray, Fl. ii. 177. *Diplopappus? occidentalis*, Hook. & Arn. Bot. Beech. 350. Et var. STENOPHYLLUS, Gray, l. c. *E. stenophyllus*, Nutt. — California, especially the western parts.

E. BREWERI, Gray, Proc. Am. Acad. vi. 541. — Sierra Nevada, in woods.

\* \* Texano-Neo-Mexicanæ, humiles; caulibus a basi ramosis; pappo duplici.

E. BIGELOVII, Gray, Bot. Mex. Bound. 78. — On the Rio Grande near Fronteras, Wright, Bigelow.

4. Species occidentales, haud canescentes; caulibus foliosis ima basi herbaceis; capitulis subcorymbosis; bracteis involucri æquilongis; ligulis 15-50.

E. CORYMBOSUS, Nutt. in Trans. Am. Phil. Soc. n. ser. vii. 308. Ligulæ 30-50, lineares, violaceæ. Pappus exterior e squamellis setulise minutis. — Rocky Mountains of Wyoming to Washington Terr. and E. California.

E. DECUMBENS, Nutt. l. c. Ligulæ 15-40, lato-lineares, albæ vel purpurascentes. Pappus exterior vix ullus. — Idaho to Utah and the borders of California.

5. Species argenteo-canescentes, montanæ; caulibus foliosis moncephalis 4-12-pollicaribus e caudice multicipiti lignescenti; ligulis albis circiter 50; foliis angustis; acheniis 6-10-nerviis.

E. CANUS, Gray, Pl. Fendl. & Proc. Am. Acad. viii. 650. — Northern New Mexico and E. Colorado.

*E. ARGENTATUS*, Gray, Proc. Am. Acad. 1. c. *E. cæspitosus*, Eaton, Bot. King, pro parte. — Arid interior region of S. Utah and Nevada.

6. Species montano-occidentales, humiles e caudice multicipiti lignescente vel incrassato; foliis angustis integerrimis (*E. composito* excepto); involucri haud lanato.

\* Folia filiformia, ima nunc spathulato-linearia nec ultralineam lata.

+ *Corollæ disci tubo villosa-hirsuta*: achenia 2-4-nervata: involucrium e bracteis subinæqualibus: caules sæpe ramosi, capitula speciosa sæpius albo-ligulata longius pedunculata gerentes: pappus fere simplex.

*E. STENOPHYLLUS*, Gray in Pacif. R. Rep. iv. 42. — N. W. Texas, Bigelow.

*E. UTAHENSIS*. *E. stenophyllus*, var.? *tetrapleurus*, Gray, Proc. Am. Acad. viii. 650. — Arid region of S. Utah, Mrs. Thompson, Capt. Bishop, Parry, Palmer.

+ + *Corollæ disci fere glabræ*: achenia binervata.

++ Pappus simplex: caules superne sæpius ramosi foliati: ligulæ 30-80, violaceæ vel albæ.

*E. FILIFOLIUS*, Nutt.; Torr. & Gray, Fl. ii. 177. *Chrysopsis canescens*, DC. Prodr. v. 328. — British Columbia to California, in the dry interior.

++ ++ Pappus satis duplex, serie exteriori setulosa vel squamellata brevi manifesta: caules floridi sæpius simplices, superne pedunculiformes monocephali: ligulæ nunc ochroleucæ, saltem flavæ!

*E. PEUCEPHYLLUS*. Facie et involucri subimbricato *E. filifolium* simulans, pube cinerea adpressa magis strigillosa, demum glabratus; foliis filiformibus; ligulis 30-40 (lin. 2-3 longis) nunc pallide cæruleis nunc ochroleucis vel luteis; pappo exteriori squamellato. *E. ochroleucus*, Auct. pro parte, Gray, Bot. Calif. i. 328, etc. *Diplopappus filifolius*, Hook. Fl. ii. 21, ex char. — British Columbia and Idaho to the Sierra Nevada, California.

*E. OCHROLEUCUS*, Nutt. Magis hirsutus, nunc glabratus; foliis e lineari-filiformibus ad lineari-spathulata inferne hirsuto-ciliatis; capitulo majore; involucri bracteis æquilongis; ligulis plus 40 (lin. 3-5 longis) nunc albidis nunc luteis; pappo exteriori fere setuloso. — Idaho and E. Oregon.

Var. *HIRTELLUS*. Hirsutior, immo hispidus pilis patentibus; ligulis aureis. *Chrysopsis hirtella*, DC. Prodr. v. 327? — E. Oregon and Idaho. Douglas? Cusick, Nevius, Howell.

+ + Folia palmati- (rarius pinnati-) partita, radicalia, vel 2-3 in caule scapiformi monocephalo, angusta, integerrima.

*E. COMPOSITUS*, Pursh. *E. pedatus*, Nutt. — Subalpine or alpine on the Rocky Mountains, Sierra Nevada to the Arctic regions, and Greenland.

Var. *DISCOIDEUS*, Gray, Am. Jour. Sci., ser. 2, xxxiii. 237.

Var. *TRIFIDUS*. Foliis parvulis 2-3-fidis, lobis oblongis vel ovatis. — Northern Rocky Mountains.

Var. *PINNATISECTUS*. Foliis pinnati-partitis in segmenta 7-11 integerrima vel 2-3-fida. — High mountains of Colorado, Hall, Hooker & Gray, Rothrock.

+ + + Folia ex angusto-linearibus ad lanceolata, ima spathulata, omnia integerrima.

++ Virides, pube hirsuta parca vel evanida: caules simplices, 2-6 pollicares e caudice multicipiti, superne nudi, monocephali: ligulae nec numerosissimae nec angustae.

= Species alpinæ; pappo simplici; pube haud glandulosa.

*E. RADICATUS*, Hook. — A still obscure species.

*E. NANUS*, Nutt. *E. nanus* & *E. radicans*, Nutt. in Trans. Am. Phil. Soc., 1. c. — High Rocky Mountains.

*E. URSINUS*, Eaton, Bot. King, 148. *Aster glacialis*, Nutt. 1. c. — High Rocky Mountains, occurs in several forms.

= = Species alpestris; pappo exteriori setuloso parum manifesto.

*E. GLANDULOSUS*, Porter, Fl. Colorad. 60. E caudice valido caespitoso 3-5-uncialis, hispidulo-glandulosus, subscaber; caulibus scapiformibus rigidiusculis; foliis radicalibus spathulato-lanceolatis (lin. 2 latis poll. 2 longis); capitulo majusculo; involucri bracteis subinaequalibus scabro-glandulosis parum hirsutis; ligulis violaceis lin. 5 longis. — Mountains of Colorado.

++ ++ Viridulae, vix cinerae, pube tenui substrigulosa plerumque adpressa: ligulae pauciusculae (25-30) nec angustae: pappus fere simplex.

= Caules floridi simplices monocephali, sat validi, superne aphylli, capitulum majusculum superati.

*E. NEVADENSIS*, Gray, Proc. Am. Acad. viii. 649. — Sierra Nevada and adjacent mountains in W. Nevada.

Var. *PYGMÆUS*, Gray, l. c. An ambiguous form, of the higher peaks of the Sierra Nevada.

= = Caules debiles, diffusi, demum ramosi: capitula parvula, ligulis lin. 3 longis albis vel purpureiscentibus.

*E. EATONI*. Substrigoso-pubescent; caulibus e radice subfusiformi 3-9-pollicaribus; foliis lineari-lanceolatis seu angusto-linearibus (poll. 2-3 longis lin.  $\frac{1}{2}$ -2 latis) supra glabrat; involucri bracteis subhirsutis fere æqualibus. *E. ochroleucus*, Eaton, in Bot. King, 152, non Nutt. — Wind River Mountains (C. Richardson) to the Uinta and Wahsatch, at 7,000 to 10,000 feet (Watson, Eaton, M. E. Jones), and S. Utah, Palmer.

*E. TENER*. Cinereo-puberulus; caulibus exiguis laxis e caudice multicipiti; foliis spathulatis seu lanceolatis, radicalibus lamina  $\frac{1}{2}$ -2-pollicari in petiolo sat longo, caulinis superioribus linearibus parvis; involucri lin. 2 longo, bracteis inæqualibus. *E. cæspitosus*, var. *tener*, Gray, Bot. Calif. i. 328. — High mountains of Nevada and adjacent part of California; also of Central Utah, Watson, Brewer, Parry.

++ ++ ++ Cinereo-canescens, pube brevi molli vel hispidula haud adpressa: caules e caudice valido ramoso plurimi, foliosi, aut simplices aut superne ramosi, capitula mediocria pauca vel solitaria gerentes: folia latiuscula.

= Ligulæ 18-30, latiusculæ, oblongo-lineares, purpureæ, modo *Asteris*.

*E. ASPERUGINEUS*. Pube hispidula minuta cinereus; caulibus simplicibus 2-6-pollicaribus sæpius monocephalis; foliis caulinis inferioribus radicalibusque obovato-rotundis vel spathulatis (lin. 3-5 latis) petiolo longiusculo, superioribus lato-linearibus; involucri e bracteis paucis æqualibus; pappo simplicissimo. *Aster asperugineus*, Eaton in Bot. King, 142. — E. Humboldt Mountains, Nevada, Watson.

= = Ligulæ numerosæ uniseriales, albæ, nunc pallide rosæ: involucrium pl. m. villosulo-hirsutum.

a. Pappus simplex.

*E. CANESCENS*, Torr. & Gray. — Northern Rocky Mountains.

b. Pappus duplex, exterior brevis setuloso-squamellatus.

*E. CÆSPITOSUS*, Nutt. in Trans. Am. Phil. Soc. l. c.; forma parvula. *Diplopappus grandiflorus*, Hook. Fl. Bor.-Am. ii. 21, forma validior macrocephala. — Rocky Mountains from the Saskatchewan to Colorado and Utah.



++ ++ ++ Hispidæ vel hirsutissimæ pilis longis patentibus: caules simplices vel superne ramosi, foliosi, spithamæi: capitula majuscula; involucri hispido-hirsuto: ligulæ 50-60, etiam 80, longæ et angustæ, mox deflexæ: pappus aperte duplex.

*E. pumilus*, Nutt. Gen. ii. 147. Robustior; ligulis albis; pappo exteriori e setulis (vix squamellis) brevibus setis interioris vix latioribus. — Plains of Dakota to Colorado and the mountains of Utah.

*E. concinnus*, Torr. & Gray, Fl. ii. 174. Hirsutior; foliis minus rigidis; calibus sæpius ramosis floribundis; ligulis violaceis raro albis; pappo exteriori paleaceo-squamellato, paleis aut subulatis aut oblongis. Var. *condensatus*, Eaton in Bot. King, 151; forma nana; paleis pappi paucioribus latioribus. — Var. *aphanactis*, Gray, Proc. Am. Acad. vi. 540: ligulis abortivis vel brevissimis, vel fl. femineis plane nullis. — Arid districts, Rocky Mountains to the Sierra and Cascades, and from Brit. Columbia to Arizona.

7. Species alpinae vel alpestres: folia latiora fere semper integerrima: involucri laxi lanosissimi pilis longissimis multiseptatis: achenia sæpius binervia: ligulæ ad 100 angustiusculæ: pappus fere simplex.

*E. uniflorus*, L. — Alpine region of the Rocky Mountains and Sierra Nevada, north to the Arctic coast.

*E. grandiflorus*, Hook. Fl. Bor.-Am. ii. 18, t. 123. — Alpine and alpestrine regions of the Rocky Mountains.

Var. *lanatus*. Depressus, ad *E. uniflorum* tendens, sed involucri squarroso-patente nec adpresso, foliis latioribus rarissime trifidis. *E. lanatus*, Hook. l. c. 17, t. 121. — High alpine summits.

Var. *elatior*, Gray, Am. Jour. Sci., ser. 2, xxxiii. 237. Caule sæpius pedali apice ramoso 2-5-cephalo folioso; foliis aut oblongis aut ovato-lanceolatis basi lata sessili. — Alpestrine, along streams in the Rocky Mountains of Colorado, first collected by Dr. Parry.

8. Species sylvaticæ vel agrestes, paucae alpestres, latifoliæ: caules foliosi, superne ramosi, raro monocephali, basi nec flagelliformi nec repentes: involucrium haud lanatum: ligulæ plerumque violaceæ vel purpureæ.

\* Capitula maxima (disco pollicem diametro) caules breves lignescentes decumbentes terminantia: pappus fere simplicissimus: ligulæ numerosissimæ et latiusculæ.

*E. glaucus*, Ker.; Torr. & Gray, Fl. ii. 172, ubi synonym. — Seashore of Oregon and California.

\*\* Capitula majuscula, disco semi-vel 3-pollicari: ligulæ 100 vel plures, angustæ: caules erecti, 1-2-pedales: folia integerrima: pap-



pus exterior manifestus, setulosus vel subulato-squamellatus. (Species nimis affines.) — § *Phænactis*, Nutt. in Trans. Am. Phil. Soc. l. c. pro parte.

*E. SPECIOSUS*, DC. — Brit. Columbia to Oregon near the coast.

*E. MACRANTHUS*, Nutt. l. c. Involucrum glabrum vel subglabrum: capitula nunquam magna. — Rocky Mountains from Wyoming to S. Utah and New Mexico.

*E. GLABELLUS*, Nutt. Gen. ii. 147. *E. asper*, Nutt. l. c. — Saskatchewan and Minnesota to the Rocky Mountains, southward to Colorado and Utah. A polymorphous species as here received. The annexed is an ambiguous form, which but for the involucre would be appended to the foregoing.

Var. *MOLLIS*, Gray, Proc. Acad. Philad. 1863, 64. Pube (etiam involucri) brevi molli patente subcinereus; caule folioso. — Colorado Rocky Mountains, at 8,000 to 9,000 feet.

\* \* \* Capitula majuscula vel mediocria: ligulæ minus numerosæ 50–70 vel pauciores, latiusculæ: corollæ disci sursum paullo ampliatae, dentibus majoribus: pappus simplex: caules erecti mono-oligocephali: folia inferiora quandoque parce serrata. Transitus ad *Asterum*.

+ Subalpinæ vel alpestres, occidentales, foliis læte viridibus: caules e rhizomate haud stolonifero subpedales ad bipedales, macriores (4–8-pollicares) monocephali.

*E. SALSUGINOSUS*. Rhizomatibus brevibus crassiusculis; foliis glabris vel subglabris oblongis seu lanceolatis, imis obovatis vel spathulatis, superioribus apiculato-acuminatis, summis subulatis: involucro laxo glanduloso-pubero seu viscido, bracteis attenuatis apice patentibus; ligulis purpureis seu violaceis. *Aster salsuginosus*, Richards. App. Frankl. ed. 2, 32; Hook. Bot. Mag. t. 4942. *A. Unalaschensis*, Less. in Linn. vi. 124. — Var. *ANGUSTIFOLIUS*: forma macra, angustifolia, Californica. — Wet ground, Kotzebue Sound to northern Rocky Mountains and subarctic plains eastward, along the higher mountains to California, Utah, and New Mexico.

Var. *HOWELLII*. Caule magis æqualiter folioso; foliis ovatis eximie acuminulatis; ligulis tantum 30–35 latioribus albis. — Cascade Mountains, Oregon, May, 1880, Joseph and T. J. Howell.

*E. COULTERI*, T. C. Porter. Rhizomatibus gracilibus; foliis pubescenti-hirsutis vel glabris pallide viridibus sæpius oblongis parce acute denticulatis vel integerrimis; involucri bracteis minus attenuatis vix patentibus undique vel basi villosis et glandulosis; ligulis angusti-

oribus albis vel purpureo tinctis. — Porter & Coulter, Fl. Colorad. 61; Rothrock in Wheeler Rep. vi. 154. — Rocky Mountains of S. Colorado, at 10,000 to 11,300 feet, Coulter. Wahsatch Mts., M. E. Jones, Rothrock. S. Utah, Ward. Sierra Nevada, California, Bolander, Greene, Lemmon.

+ + Orientalis, stolonifero-caespitosus; capitulis mediocribus paucis umbellato-cymosis rariusve solitariis.

*E. BELLIDIFOLIUS*, Muhl. — Canada to Louisiana, west to Illinois. There are indications of an allied species in Oregon.

\* \* \* \* Capitula minora (disco lin. 3-4 lato) pl. m. cymosa: ligulae numerosissimae, angustae, purpureae vel purpurascentes: pappus simplex: plantae sparsae e surculis stolonibus filiformibus provenientes perennantes (vel biennes?).

*E. PHILADELPHICUS*, L.; Torr. & Gray, Fl. ii. 171, ubi synonym. — Nearly throughout the United States and British America.

*E. QUERCIFOLIUS*, Lam.; Torr. & Gray, l. c., ubi synonym. — S. Carolina to Texas.

9. Species humiles, caulibus repentibus seu ramis procumbentibus foliosis apice radicanibus perennantes: ligulae numerosissimae, angustae, pallidae: capitula solitaria, longe vel scaposo-pedunculata: pappus e setis pauciusculis.

\* Pappus simplex: folia saepe undulato-dentata seu lobata.

*E. SCAPOSUS*, DC. Prodr. v. 287; Benth. Pl. Hartw. 17. *E. longipes*, DC. l. c. 285. *Aster rivularis*, Schlecht. — Mexico.

Var.? *CUNEIFOLIUS*. Hirsuto-pubescent; ramis plerisque prostratis repentibus; pedunculis axillaribus scapiformibus; foliis cuneatis vel obovatis obtusis obtuse grosseque 5-9-dentatis, basi angustata integerrima; pube cinerea adpressa; involucri lin. 4 diametro. *E. scaposus*, Torr. & Gray, Fl. ii. 170; Gray, Pl. Lindh. i. 11 (vix var. latifolium DC. ex char.). — Sandy sea-shore, Texas.

\* \* Pappus duplex, exterior subulato-setulosus: caules floridi scapiformes, steriles flagelliformi-procumbentes, foliosi, apice demum radicales et proliferi: folia integerrima, caulina angusta.

*E. FLAGELLARIS*, Gray, Pl. Fendl. 69. — W. Texas to New Mexico, S. Utah, Colorado.

Series 2. Species annuae vel biennes, vix unquam montanae.

\* *Achenia angusta minus compressa, apice truncato albo-coronulato: pappus simplex.*

*E. BELLIDIASTRUM*, Nutt. Trans. Am. Soc. l. c. — Low plains of Nebraska to New Mexico.

\* \* *Achenia compressa* generis : pappus duplex, exterior brevissimus, setulis squamellisve numerosis nunc in coronulam pl. m. concretis. — § *Phalacroloma*, Torr. & Gray, Fl.

+ Pappus conformis : folia pleraque integerrima : plantæ humiles.

++ Ligulæ 30–40, albæ.

*E. MODESTUS*, Gray, Pl. Fendl. 68, excl. syn., & Pl. Lindh. ii. 220. — Sterile plains, W. Texas.

++ ++ Ligulæ circiter 100, angustæ.

*E. DIVERGENS*, Torr. & Gray, Fl. ii. 175, et var. *CINEREUS*. *E. cinereus*, Gray, Pl. Fendl. *E. nudiflorus*, Buckley in Proc. Acad. Philad. — Nebraska to California and Mexico.

*E. TENUIS*, Torr. & Gray, l. c. — Arkansas, Louisiana, and Texas, in low grounds.

+ + Pappus interior setosus in radio nullus, vel parcissimus caducus : ligulæ 50–80, albæ, nunc purpurascens (lin. 3 longæ) : caules erecti, 1–4-pedales, folia plurima indivisa et capitula parvula sat numerosa gerentes. — *Phalacroloma*, Cass.

*E. ANNUUS*, Pers. ; Torr. & Gray, l. c. ubi synonym. — Canada to Virginia and west to Oregon.

*E. STRIGOSUS*, Muhl. ; Torr. & Gray, l. c. — Canada and Saskatchewan to Texas and California.

Var. *BEYRICHI*, Torr. & Gray. — Arkansas and Texas.

+ + + Pappus radii ut disci perfectus, interior caducus, exterior e squamellis insigniter concretis : folia caulina pinnatipartita : ligulæ numerosissimæ angustæ. — *Stenactis*, Cass. *Polyactis*, Less. *Polyactidium*, DC.

*E. DELPHINIFOLIUS*, Willd. New Mexico, Arizona, Mexico.

§ 2. *TRIMORPHÆA*. Flores feminei sæpissime biformes, exteriores angustissime et breviter aut brevissime ligulati, interiores corolla filiformi tubulosa stylo multo brevioribus : folia subintegerrima. — *Trimorphæa*, Cass.

\* Caules humiles sæpius monocephali e rhizomate perenni : ligulæ exsertæ, tubo pilis parvis elongatis pluriseptatis instructo.

*E. ALPINUS*, L. — Alpine region of the northern Rocky Mountains, Drummond.

- \* \* Caules spithamæi ad sesquipedales e radice bienni vel subperenni, majores ramosi oligo-polycephali: ligulæ parum exsertæ vel inclusæ.

+ Purpureæ: corollæ eligulatæ filiformes numerosæ.

*E. ACRIS*, L. — Anticosti and Labrador to the Rocky Mountains, south to Colorado and Utah, and to the northwest coast.

Var. *DREBACHENSIS*, Blytt, Norg. Fl. 561. Glaber vel subglaber; involuero nudo vel basi tantum hirsuto; ligulis aut subexsertis aut minutis filiformibus pappo etiam per anthesin brevioribus. *E. elongatus*, Ledeb. Fl. Alt. *E. Kamtschaticus*, DC. Prodr. *E. glabratus*, Hook. Fl. Bor.-Am. ii. 18, maxima parte, non Hoppe. — Same distribution, and numerous intermediate forms.

+ + Albidæ, filiformes: flores interiores eligulatæ haud visæ!

*E. ARMERIÆFOLIUS*, Turcz. *E. lonchophyllus* & *E. glabratus* var. *minor*, Hook. *E. racemosus*, Nutt. — Saskatchewan and along the Rocky Mountains to Colorado, the Wahsatch, and the Sierra Nevada.

§ 3. *CENOTUS*, Nutt. Flores fœminei uniformes numerosi; ligulis inconspicuis semper tubo suo brevioribus, aut parum exsertis stylum vix superantibus, aut minimis etiam obsoletis: flores disci sæpius pauci, corolla quadridentata: herbæ annuæ et biennes, microcephalæ. (Transitus ad *Conyzam*.)

- \* Floccoso-lanatæ, incanæ, nec viscida vel hirta: pappus simplex.

*E. ERIOPHYLLUS*, Gray, Pl. Wright. ii. 77. — S. Arizona.

- \* \* Leviter arachnoideæ, mox nudatæ, pube subviscida.

*E. SUBDECURRENS*, Schultz Bip. *Conyza subdecurrens*, DC. Prodr. v. 379. *C. Coulteri*, Rothrock in Wheeler Rep. vi. 155, non Gray. — S. Arizona on Mt. Graham, Rothrock. Mexico, recently collected by Schaffner, Parry, and Palmer.

- \* \* \* Pube nec lanata nec viscida hirsutæ vel hispidæ: caules foliosisimi.

+ Inquilineæ, involuero cinereo-pubescente.

*E. LINIFOLIUS*, Willd. *E. ambiguus*, Schultz Bip. in Phyt. Canar. *E. Bonariensis*, DC. pro parte. *Conyza ambigua*, DC. *C. sinuata*, Ell. — Waste grounds, coast of S. Carolina to Florida.

+ + Indigenæ, microcephalæ, involuero fere glabro.

*E. CANADENSIS*, L. — Everywhere common, now a cosmopolite weed.

*E. DIVARICATUS*, Michx. — River-banks of the Mississippi and its tributaries, to Texas.

**ASTER.** The revision of this vast genus is not yet completed, owing to the great difficulty which is experienced in settling the synonymy and the limits of some of the earlier as well as of the later known species. It is intended to accept the genus in the wide extent assigned to it in the *Genera Plantarum* of Bentham and Hooker, at least so far as North America is concerned, and also to include *Brachyactis*. The subgenera may be arranged in two series; the first of perennials, the second of annuals and biennials; and an endeavor has been made to dispose of the perennial Asters under the following subgenera.

§ 1. **AMELLASTRUM**, best marked by its broad and obovate very flat achenia with callous-nerved or thickened margins, and no lateral nerves. Here *A. alpinus* and the variety *flaccidus*, and the wholly Old World *A. Amellus*, L.

§ 2. **MEGALASTRUM**. This was indicated in Pl. Wright. ii. 75, and it connects the genus with *Townsendia*. The head, as the name denotes, is very large, and the leading character is found in the unusually coarse and rigid bristles of the pappus. The species are *A. tortifolius*, Gray (*Aplopappus tortifolius*, Torr. & Gray), and *A. Wrightii*, Gray (*Townsendia* § *Megalastrum Wrightii*, Gray in Bot. Mex. Bound. 78), Texano-Arizonian species, more or less suffrutescent.

§ 3. **HELEASTRUM**. DeCandolle's genus of that name, well restored as a section by Bentham, which also has unusually coarse and rigid pappus-bristles, the stronger ones somewhat clavellate at tip; the coriaceous-foliate bracts of the involucre are somewhat equal in length; the achenia narrow, mostly slender, little compressed, and 8-10-nerved. *A. eryngiifolius*, Torr. & Gray, and *A. spinulosus*, Chapman, are referred here, along with the original *A. paludosus*, Ait. All three are low pine-barren species of the Southern Atlantic States.

§ 4. **HESPERASTRUM** was indicated in the Botany of California, under § *Machæranthera*. The single species, *A. Shastensis*, of Mt. Shasta, California, is truly perennial, has narrow and hardly at all compressed achenia traversed by 5 strong nerves and intermediate striæ; but the pappus is soft. The leading peculiarity is in the neutral rays, after the manner of *Corethrogyne*, of which it has somewhat the habit. But the style-appendages are slender and naked.

§ 5. **BIOTIA**, a well known group, with appendages to the involucral bracts so short or obscure that the section might be placed next to the sections *Dællingeria* and *Orthomeris*, while on the other hand it is nearly related to *Sericocarpus*, also to the *Calliastrum* group of the

§ 6. EUASTER, or ASTER PROPER. This includes all the remaining perennial Asters which have partly herbaceous or foliaceous, or at least herbaceous-tipped involucre bracts, and a simple pappus.

§ 7. DELLINGERIA, adopted from Bentham and Hooker, is marked by the short involucre of thin coriaceous inappendiculate bracts, and a double pappus, the outer like that of many species of *Erigeron*, the larger bristles of the inner commonly clavellate-thickened at apex; the rays, as in § *Biotia*, are few. *A. infirmus*, Michx. (a somewhat earlier name than *A. cornifolius*, Muhl.), *A. umbellatus*, Mill. (which includes *A. amygdalinus*), and the somewhat ambiguous *A. reticulatus*, Pursh, are the species.

§ 8. IANTHE, taken from Torr. & Gray, Fl., includes a few species with pappus inconspicuously double, the outer being slender-setulose or indistinct, the bristles of the inner not at all clavellate; the involucre, &c. that of the following section. (*A. obovatus*, Meyer, the *Rhinactina limonifolia*, Less., lies between this section and the preceding.) Our species are *A. linariifolius*, L., *A. scopulorum* (the *Chrysopsis alpina* and *Diplopappus alpinus* of Nuttall), and *A. ericæfolius* from Rothrock, which is the *Diplopappus ericoides* of Torrey and Gray.

§ 9. ORTHOMERIS is taken from Torrey and Gray, Fl., with some extension. It includes the remainder of our perennial Asters, those with simple pappus and no green tips to the involucre bracts. *A. acuminatus*, Michx., and *A. nemoralis*, Ait., make the first section. Another consists of *A. Engelmanni*, Gray, *A. ledophyllus* (promoted from the variety of the preceding), and *A. elegans*, Torr. & Gray, three very close species, and *A. glaucus*, Torr. & Gray. *A. ptarmicoides*, which forms another section, has a var. *Georgianus*, remarkably tall and branching, from the mountains of Georgia, where Dr. Chapman collected it; the *Xylorrhiza* section has a proposed new species, *A. Watsoni*, founded on a plant referred to *A. glacialis* by Eaton in Bot. King (no. 509): it may pass into *A. arenarioides*, Eaton. The remaining section consists of species which had been referred to *Oxytripolium*. The last of them is *A. tenuifolius*, L. (not of subsequent authors), which is *A. flexuosus*, Nutt., and which differs from the following only by the perennial rootstock.

The series of monocarpic (annual and biennial) Asters contains the following subgenera or primary sections, besides *Tripolium* of the Old World.

§ 10. OXYTRIPOLIUM. *Tripolium* § *Oxytripolia*, DC., excluding the perennial species. It is suspected that the widely distributed warm-

temperate species for which Nuttall's specific name of *divaricatus* was adopted by Torrey and Gray is *A. exilis* of Elliott. *A. subulatus*, Michx., is a name for the other species preferred to *A. linifolius*, L.; for the true original of the Linnæan plant is a *Galatella*. This species, with its inconspicuous rays, hardly surpassing the disk and commonly surpassed by the mature pappus, and with its fewer disk-flowers, must be held to invalidate the genus *Brachyactis*, which is

§ 11. *CONYZOPSIS*, Torr. & Gray. This name having been used in this sense, as the name of a section, before the generic name *Brachyactis* was published, should be continued by those who do not admit the latter genus. It is, as it were, the analogue of the section *Trimorphæa* in *Erigeron*. The American species are *A. frondosus* and *A. angustus*, Torr. & Gray. *Brachyactis robusta*, Benth., by its involucre, flat and nerved-margined achenia, and no ligules, appears to be a *Conyza*; besides its pappus is distinctly double. *B. menthodora*, Benth. (Hook. Ic. Pl. t. 1106) seems to be a true perennial *Aster*.

§ 12. *MACHÆRANTHERA*. One division of this is the genus *Machæranthera* of Nees; the other is the genus *Dieteria* of Nuttall. Except for the biennial or annual root, and the disposition to have spinulose-toothed or cleft or dissected leaves, this subgenus would rank among the true *Asters* in the early part of the first series. *A. gymnocephalus* (*Aplopappus*, DC.) is a common Mexican species. As we receive it *A. canescens*, Pursh, would appear to comprise three or four species, the extreme forms being widely different. These are arranged as varieties, under the heads of var. *viridis* (the *Machæranthera canescens*, var. *glabra*, Gray, Pl. Wright. i. 89, etc.); var. *latifolius* (*M. canescens*, var. *latifolia*, Gray, Pl. Wright. ii. 75, and *Dieteria asteroides*, Torr. in Emory Rep. 142); var. *viscosus*, to which belongs *Dieteria viscosa* and *sessiliflora*, Nutt., and *D. incana*, Torr. & Gray (*Diplopappus incanus*, Lindl. Bot. Reg. t. 1693, & Hook. Bot. Mag. t. 3382); and var. *tephrodes*, of Southern California, Arizona, and New Mexico, which was named *A. incanus* in the Botany of California, but which cannot be Lindley's plant.

Among the true *Asters* are several forms which have to be named, such as *A. Porteri* for *A. ericoides*, var. *strictus*, Porter & Coult. Fl. Colorad. 56, and *A. Pringlei*, from the northern end of Lake Champlain,—species allied to *A. ericoides*. One species of Oregon is so well marked that it may here be characterized:—

**ASTER CUSICKII.** Cinereo-pubescent, pube molli nec scabra; caulibus simplicibus vel apice ramosis 1-2-petalibus usque ad capitula solitaria majuscula foliosis; foliis amplis (inferioribus poll.



3-4, summis 2-3 longis) membranaceis parce denticulatis vel integerimis, radicalibus caulisque infimis spathulato-obovatis in petiolum alatum basi auriculato-dilatatum amplexicaulem angustatis, cæteris ovatis oblongisve acutatis basi cordato-amplexicaulibus; involucrio hemisphærico foliaceo discum æquante, bracteis extimis foliis referentibus intimas lanceolatas superantibus; ligulis numerosis angustis pallide cæruleis semipollicaribus; acheniis glabris. — Along streams in the subalpine region, in the mountains of Union Co., E. Oregon, W. Cusick.

Whether *Galatella*, DC. (*Galatea*, Cass.) should be kept distinct from *Aster*, partly for geographical reasons, may be still a mooted question; but whether as a genus or subgenus it could hardly include a West-Indian shrubby plant, which has been mistakenly referred to *Solidago*. It is proposed now to distinguish it, under the name of

**GUNDLACHIA**, Nov. Gen. *Asteroidæarum*. Capitulum pauciflorum, heterogamum; floribus radii 1-3 fœminei; disci 3-5 hermaproditis, omnibus fertilibus. Involucrum angustum; bracteis siccis gradatim imbricatis subcarinatis uninerviis; intimis lato-linearibus, extimis brevibus subovatis. Corolla radii ligula alba oblonga discum æquante; disci flava, limbo usque ad tubum gracilem 5-partito, lobis linearibus patentissimis. Stamina prorsus exserta. Styli fl. herm. rami plani, appendice fere æquilonga et lata acutiuscula superati. Achenia gracilia, teretia, 5-nervia. Pappus uniserialis, e setis copiosis capillariibus æqualibus. — Frutex orgyalis, ramis erectis foliosissimis linearibus subtrinerviis integerrimis, capitulis *Solidagini* referentibus, sed in thyrsum paniculæformem vel subcorymbiformem (nec racemiformem) digestis.

**GUNDLACHIA DOMINGENSIS.** *Solidago Domingensis*, Spreng. Syst. iii. 639; DC. Prodr. v. 341; Griseb. Cat. Cub. 150. *S. Lindeniana*, A. Rich. fide Griseb. *Baccharis ptarmicæfolia*, Griseb. in Pl. Wright. Cub. 513 (no. 1314), non DC. — St. Domingo, Bertero. Cuba, Linden, Wright, toward the eastern end of the island. Dedicated to Mr. J. Gundlach of Havana, an acute naturalist, the friend and companion of Charles Wright in his Cuban explorations.

The following are the characters of a few new *Compositæ*.

**CHENACTIS SUFFRUTESCENS.** Albo-tomentosa; ramis floridis e caule perenni lignescente decumbente vel humifuso erectis (subpedalibus) apice longe nudis pedunculiformibus monocephalis; foliis in segmenta 5-7 linearia obtusa subintegerrima 1-2-pinnatipartitis; in-



volucro (subpollicari) denudato viscidulo, bracteis linearibus obtusis; corollis homomorphis albis pappo simplici 10-12-paleato paullo longioribus. — Rocky banks of the Sacramento below Mount Shasta, California, Lemmon.

**ACTINOLEPIS LEMMONI.** Tenella, laxe ramosa, triuncialis, lana tenui floccosa decidua demum glabrata; foliis parvis alternis fere linearibus obtusis integerrimis carnosulis; capitulis (lin. 3 longis) pedunculatis angustis; involucro e bracteis 6-7 oblongis; receptaculo plano; ligulis 4-6 lato-ovalibus tridentatis roseo-albis discum vix superantibus; acheniis clavatis hirsutis; pappo nullo. — Mohave Desert, S. E. California, on the borders of Arizona, Lemmon, 1880.

**LAPHAMIA LEMMONI.** Parva, ramosa, depressa, subcinereo-pubescent; foliis omnibus oppositis cordato-rotundis (cum petiolo fere æquilongo semipollicaribus) 5-7-lobatis incisive nunc fere partitis, lobis obtusissimis; pedunculis capitulo haud longioribus; involucri bracteis lineari-oblongis vel subspathulatis obtusissimis subplanis; ligulis nullis; corollis disci luteis; styli ramis elongato-subulatis; acheniis compressiusculis pube brevi densa subcinereis; pappo uni- (raro bi-) aristellato sæpe evanido. — Near Camp Lowell, Tucson, Arizona, Lemmon, 1880. — Depressed-spreading, only 2 or 3 inches high; the heads 4 lines high. The usually solitary bristle of the pappus is exceedingly slender, about the length of the proper corolla-tube and half that of the achenium; rarely there are two contiguous ones, in many flowers none at all or a mere rudiment. Assuming a form with incisely lobed leaves as the type, a marked variety, sent under a separate number, from the same station, is to be indicated, viz.: —

**Var. PEDATA.** Foliis plerisque pedatipartitis vel bipalmatifidis. — With the typical form.

**FLEISCHMANNIA SCHAFFNERI.** Suffruticosa, humilis, viscidulo-pubescent, odore moschato; foliis plerisque alternis tenuiter petiolatis biternatipartitis, lobis sublinearibus 2-3-dentatis dentibusque acutis calloso-apiculatis; capitulis longe pedunculatis; involucro glabro pluriseriali; corollis albidis; stylis læte roseis prælongis; pappi setis 5-6. — Shaded and humid ground, in the mountains near San Francisco (San Luis Potosi), Mexico, Dr. J. G. Schaffner, Aug., 1876, no. 349.

**EUPATORIUM MYGINDÆFOLIUM.** Fruticosum, depressum, subpedale, glutinosum, glabrum; foliis crebis oppositis oblongis (semipollicem longis) obtusiusculis basi in petiolum attenuatis utrinque 1-4-dentatis vel denticulatis crasso-coriaceis subaveniis triplinerviis; capitulis subsolitariis ramulos terminantibus inter folia sessilibus 15-

floris; involucri (lin. 4 longo) e bracteis 7-8 oblongo-lanceolatis acutiusculis paucinerviatis floribus (albis?) paullo brevioribus biseriatis, exterioribus parum brevioribus; acheniis secus costas hispiduloscabris. — Province of San Luis Potosi, on high mountains near San Miguel, Dr. J. G. Schaffner, coll. Aug. 1876.

*PHILACTIS LONGIPES*, Gray, Proc. Am. Acad. xv. 35, is now received from Dr. Schaffner, the specimens in a more advanced state, showing the obpyramidal-triangular fertile akenes of the ray, the inner angle usually aristellate; and the akenes of the disk, though seemingly well formed, are infertile.

## II. *Some Species of Asclepias.*

In the conspectus of the species of *Asclepias* published in these Proceedings (vol. xii.), and in the Synoptical Flora of North America, two undescribed species lurked undetected, one under *A. longicornu*, the other under *A. brachystephana*. Both of them were brought to light and are named by the Rev. Edward L. Greene, one of our keenest observers, who collected and examined the living plants in the interesting field where he is now stationed in New Mexico. The main characters of these species are appended.

*ASCLEPIAS WRIGHTII*, E. L. Greene, in litt. *A. longicornu* & *A. nyctaginifolia* affinis, hirta-puberula, viridiflora: caulibus e radice crassa decumbentibus spithamæis et ultra foliosis; foliis lato-lanceolatis ovatisve e basi acuta petiolatis; umbellis ad plerosque nodos subsessilibus plurifloris; cucullis erectis lineari-oblongis antheris triplo longioribus basibus rotundatis columnam brevissimam obtegentibus præter margines albidas alæformes superne dilatatas solidis infra medium vix constrictis intus sub apice crista parva bifida, lobo postico obtusissimo, antico in cornu breve falcatum subinclusum producto; antherarum alis semi-ovatis. — Near Santa Rita, New Mexico, C. Wright, 1851-2. In the same district between Silver City and Lone Mountain, July 10, 1880, E. L. Greene. Mr. Wright's specimens, in fruit and with flowers in poor condition, were mixed with those of *A. longicornu* and remained unnoticed until the species was collected and well described as a new one by Mr. Greene, who assigns to it the present name. The follicles are like those of *A. longicornu*; those of *A. nyctaginifolia* are not known, but are probably of the same character. *A. Wrightii* is wholly related to the latter, but the two should be brought into proximity with *A. longicornu*, which thus becomes less isolated in the genus.

*A. UNCIALIS*, E. L. Greene in Bot. Gazette, v. 64 (1880). *A. brachystephana* quoad flores affinis, facie *A. involucrate*, sed humillima; cucullis antheris paullo brevioribus, dorso lato-rotundato lobos auriculæformes anticas æquante, cornu seu processu ovato-oblongo obtusissimo incluso. — New Mexico near Silver City, Greene. Plains of Colorado, Hall & Harbour (478). Green River, N. W. Wyoming, Parry (246). The last two have been referred to *A. brachystephana* in Proc. Acad. Philad. 1863, Am. Nat. 1874, and in Syn. Fl. ii. 94. The stems above ground are only an inch or two high, so that the name is not inappropriate, even if they should attain a somewhat greater height. As in the related *A. brachystephana*, the hoods are not higher than broad, and are of similar structure, but the back is rounder and the triangular anterior lobes or auricles not projecting, while a short fleshy process takes the place of the subulate horn. The hoods are not longer than those of *A. brachystephana*, but the *gynostemium*, or mass above the insertion of the hoods, is shorter.

*ASCLEPIAS QUINQUEDENTATA*, var. NEO-MEXICANA, E. L. Greene in litt. Floribus subdimidio minoribus. — Rocky mountain-side east of Pinos Altos, in the southern part of New Mexico, June 22, 1880, E. L. Greene. The discoverer had distinguished and characterized this as a new species, and justly, if the published character of *A. quinquedentata* were quite correct. But in that a mistake was made by assigning "a small acute dorsal tooth" to the horn of the hood. That tooth is, in fact, only the middle one of the five teeth of the hood itself, to which the horn is sometimes adnate up to the very tip, sometimes not so far. Wright's original certainly has flowers of nearly twice the size of those of Mr. Greene's specimens. But the plant growing around San Luis Potosi (Parry and Palmer's 583, and also sent by Dr. Schaffner) is just intermediate. In this species, as in *A. Linaria*, Cav., the follicle is arrect on a deflexed pedicel.

The characters of three species of adjacent Mexico are appended.

*ASCLEPIAS SCHAFFNERI*. Species concinna, *A. Coulteri* affinis, glabella; caule gracili simplici subpedali; foliis oppositis filiformi-linearibus; umbellis pedunculatis laxe paucifloris; floribus rubellis nunc viridulis; corollæ lobis (lin. 3 longis) ovato-oblongis; cucullis (cum columna brevi parum breviori) antheras sublonge superantibus complicato-compressis inferne dorso carnosissimis solidis superne petaloideis antice utrinque longe acuminato-productis, dorso quasi exciso medio callo obtuso apiculato, processu interno adnato subulato gracili rectiusculo longe exserto: folliculo fusiformi puberulo arrecto. — Near San Luis Potosi, Mexico, Schaffner, Parry & Palmer (582).

The slender horns moderately surpass the subulate-attenuate anterior lobes of the hoods. The follicle in the only fruiting specimen is erect on a circinnate pedicel.

**ASCLEPIAS PUBERULA.** Subglabra, spithamæa; foliis oppositis lanceolatis (infimis nunc oblongo-lanceolatis) seu linearibus,  $1\frac{1}{2}$ -3-pollicaribus sat petiolatis; pedunculis umbella plurifloro longioribus; corollæ albide lobis lato-ovatis supra puberis; columna brevissima; cucullis ovatis obtusissimis crassis stigma parum superantibus processu suo lingulato obtusissimo prorsus adnato vix longioribus.— In swamps, Morales, near San Luis Potosi, Schaffner.

**ASCLEPIAS EUPHORBIEFOLIA.** Engelm. in herb. Humifusa, a basi ramosa, fere glabra; foliis omnibus oppositis parvis (lin. 2-3 longis) ovatis subcordatis raro oblongis subcarnosis eveniis breviter petiolatis; pedunculis terminalibus umbellæ 7-9-floræ æquilongis; floribus roseo-albidis (lin. 2 longis); columna brevissima; cucullis ovato-oblongis obtusis basi marginibus inflexis corollæ lobis parum æquilongis infra medium processu falcato brevi incluso auctis; folliculis puberulis lævibus in pedicello arrecto-inflexis.— Near San Luis Potosi, in sandy soil, Schaffner (1876), Parry and Palmer, the latter in a single specimen.

### III. *A New Genus of Gentianaceæ.*

**GENIOSTEMON**, Engelm. & Gray.

Calyx alte 4-fidus; lobis lanceolatis carinatis subulato-acutis. Corolla marcescenti-persistens, subrotata; tubo lobis ovalibus haud longiore. Stamina 4, fauci inserta: filamenta antheris oblongis immutatis æquilonga, glanduloso-barbata. Stylus elongatus, filiformis, persistens: stigma infundibuliformi-capitatum, subintegrum. Capsula oblonga, placentis intrusis semibilocularis, polysperma. Semina subglobosa; testa conformis parum foveolata.— Herbæ Mexicanæ, annuæ? pusillæ (bipollicares), ramosæ, parvifoliæ; floribus pedunculatis cærulescentibus. *Erythrae* et *Microcalæ* affinis.

**GENIOSTEMON COULTERI.** Caulibus teneribus parum ramosis æqualiter foliatis; ramis unifloris; foliis spathulato-lanceolatis (lin. 3 longis) basi attenuatis; pedunculo flore haud longiore; filamentis infra medium creberrime glanduloso-barbatis; antheræ loculis utrinque obtusis (corolla lin. 4 longa, ut videtur alba?).— Mexico, Coulter, no. 945.

**GENIOSTEMON SCHAFFNERI.** E radice forte annua multicaulis, cymoso-ramosissimus et multiflorus; foliis linearibus (lin. 2-3 longis)

imisve spathulatis, summis subulatis basi haud angustatis; pedunculis gracilibus flore longioribus; filamentis sub apice barbatis inferne nudis; antheræ loculis basi subacutis (corolla cærulescente). — In mountain swamps, San Luis Potosi, Schaffner.

#### IV. *Miscellanæ of the North American Flora.*

**ASTRAGALUS GREENEI.** *Phaca*, inter *Inflatos* et *Scytocarpos*, subpedalis e radice perenni, cinereo-pubescens; stipulis deltoideo-subulatis; foliis multijugis obovatis oblongisve retusis confertis (lin. 3 longis); pedunculis folio longioribus; spica oblonga confertim multiflora; floribus lin. 4 longis parvibracteatis brevissime pedicellatis patentibus; calyce campanulato pilis nigricantibus albidisque sericeo-hirsutis, dentibus angustis subacutis tubo dimidio brevioribus; corolla purpurea basi alibda, carina obtusissima; legumine turgido ovali semipollicari cinereo-puberulo prorsus uniloculari in calyce sessili polyspermo. — Foothills of the Mogollon Mountains, New Mexico, April 20, 1880, E. L. Greene.

Some other *Astragali* remain to be characterized; and a new conspectus of the North American species will be needed.

**DALEA WISLIZENI**, Gray, Pl. Fendl. var. *sessilis*. *Lateriflora*; spicis brevibus sessilibus ramulos breves foliosos secus caules prolixè dispositos terminantibus. — New Mexico and Arizona, Greene, 1877, Lemmon, 1880.

**SEDUM MEEHANI.** Glaucescens, 2-3-pollicare, radicibus fibrosis perennans, foliosum; foliis teretibus (subsemipollicaribus, floralibus minoribus); ramis calycibus ovariisque tenuiter glanduloso-hirtellis; floribus omnibus 5-meris; petalis albis (lin. 2 longis) lanceolato-ovatis tenuiter acuminatis calycis lobis ovatis plus duplo longioribus. — Utah, on City Creek, north of Salt Lake City, at the base of the mountains, coll. by Mr. John Reading, the live plant communicated by Professor Thomas Meehan. It is so desirable to connect in this way the name of Mr. Meehan with the botany of the country which he has done so much to illustrate, that the actual collector will probably join us in wishing it to be commemorated by this pretty little species of *Sedum*. It will not make much show among Meehan's "Flowers of the United States Illustrated," of which four goodly volumes have already appeared under his editorship; but it is to be hoped that it will find a place in the fifth volume.

**DOUGLASIA LÆVIGATA.** *Depressa*; pedunculo pedicellisque puberulis, cæterum glaberrima; foliis oblongo-lanceolatis obtusis crassis

haud ciliatis in caudicibus rosulatis; umbella simplici (nec prolifera) 2-5-flora; calycis lobis deltoideo-ovatis tubo suo æquilongis tubo corollæ brevioribus; corollæ lobis latis tubo suo subdimidio brevioribus. — On Mount Hood, Oregon, May, 1880, Joseph and T. L. Howell. A handsome and well-marked species of an interesting genus, to stand next to the little known *D. arctica*.

**ECHINOSPERMUM HISPIDUM.** E caudice perenni erectum, pedale, setis asperis patentibus hispidum; foliis lanceolatis, imis oblongis in petiolum attenuatis; racemis sub-ebracteatis paniculatis laxis; pedicellis calyce longioribus, fructiferis decurvis; corolla rotata viridulo-alba intus basi annulo prominulo instructa; nuculis dorso planis breviter parceque glochidiatis, margine ala submembranacea dentata cinctis, dentibus subulatis apice glochidiatis. — Northeastern Oregon, on Rocky hillsides of Pine Creek, June, 1880, Cusick. In flower and with forming fruit. This would belong to Boissier's genus *Paracaryum*, as that genus is defined and limited by Bentham, better indeed than does *E. glochidiatum*. But however it be for the species which in the Genera Plantarum are referred to *Rindera*, these two species cannot well be separated from *Echinospermum*. *E. Redowskii* var. *cupulatum* is instructive in this respect. The flowers are no larger than those of *E. deflexum*.

**PENTSTEMON CUSICKII.** *Saccanthera*, *P. Kingii* proximus, pruinoso-puberulus (sub lente), nec glandulosus; caulibus e basi frutescente strictis gracilibus (subpedalibus) foliosis; foliis anguste linearibus; pedunculis thyrsi pluriflori gracilibus; sepalis ex ovato acuminatis; corolla semipollicari læte purpureo-cærulea; filamento sterili apice dilatato. — On the banks of Powder River or Eagle Creek, N. E. Oregon, June, 1880, Cusick. A neat and pretty species, related to *P. Roezli* and yet more to *P. Kingii*, but manifestly distinct, dedicated to the worthy discoverer.

**GILIA DEPRESSA,** Marcus E. Jones. E radice annua divaricato-ramosa, demum humifuso-depressa, pilis brevibus multiseptatis cinereo-hirsutula, viscidula; ramis ad apicem usque æqualiter foliatis; foliis oblongo-lanceolatis (semi-ad subpoll.) utrinque attenuatis integerrimis vel inciso-1-2-dentatis, dentibus apiceque cuspidate tenui mucronatis; floribus subsparsis brevipedunculatis; calycis 5-partiti segmentis e basi lata sensim attenuato-subsetigero-acuminatis corolla hypocraterimorpha albida parum brevioribus capsulam ovoideam superantibus; corollæ lobis ovalibus tubo 3-4-plo brevioribus, sinu unico paullo profundiore; staminibus tubo supra medium insertis e fauce parum exsertis; seminibus in loculis 4-5, testa mucilaginosa haud

spirillifera. — In sand at Deseret, S. Utah, June 16, 1880, Marcus E. Jones. Most related to *G. pumila* and *G. polycladon*, which are ambiguous between the *Elaphocera* and the *Eugilia* sections. The slight irregularity in the depth of the sinuses of the corolla is of little account.

REVERCHONIA, Nov. Gen. *Euphorbicearum*.

*Phyllanthea*, *Phyllantho* affinis, verum-tamen antheris introrsis, ovulis amphitropis, seminibus adscendentibus, cotyledonibus *Stenolobicearum* angustis. — Flores dioici et monoici. *Masc.* Calyx 4-partitus; segmenta spatulato-oblonga, subherbacea, æstivatione leviter imbricata. Discus obscurus. Stamina 2, sepalis totidem opposita: filamenta brevina, distincta: antheræ immutæ, introrsæ, loculis contiguïs parallelis longitrorsum dehiscentibus. *Fœm.* Calyx 6-partitus; segmenta maris similia. Discus pateriformis 6-crenatus. Ovarium triloculare; styli breves, discreti: stigmata brevina, crassa, emarginato-biloba. Ovula in loculis gemina, amphitropa, medio inserta. Capsula trilocularis, globosa, primum subcarnosa, demum in coccos bivalves dissiliens. Semina in loculis bina, supra basim hilo parvo inserta, adscendentirecta, sectione transversa trigona dorso convexa, estropholata; testa crustacea. Embryo in albumine carnoso parum incurvus, teres; radícula supera, gracilis, cotyledonibus angustis parum latioribus longior.

REVERCHONIA ARENARIA. Herba annua, parvula, glabra, patentim ramosa; foliis alternis brevi-petiolatis oblongis vel angustioribus integerrimis crassiusculis (semi-sub-pollicaribus); stipulis lato-subulatis scariosis; floribus fœmineis brevipedicellatis aut in axillis solitariis aut in plantis androgynis singulo in fasciculo paucifloro pl. masc.; perianthio viridulo demum purpurascente. — Sandy river-banks of W. Arkansas and N. W. Texas. Sand-hills along the Canadian, Dr. J. M. Bigelow, Sept. 10, 1853. Sand-hills of the Brazos, Baylor Co., Texas, Julien Reverchon, September, 1879.

Of this interesting plant, both collectors obtained only the female plant, and in fruit. But Mr. Reverchon has raised a plant or two from seed. The latter prove to be sometimes monœcious and androgynous. The late Dr. Torrey had ascertained the carpological characters, except as to the embryo, from Dr. J. M. Bigelow's specimens. The rediscovery enables me to complete the character, and to establish on it a new genus; which, with great satisfaction, I dedicate to M. Julien Reverchon, of Dallas, Texas, the second discoverer, — a valuable correspondent, an acute and sedulous botanist.

The relationship of this plant to *Phyllanthus* is so close, that, were



it not for a combination of characters, it might be taken for an aberrant *Phyllanthus*. Although the cotyledons are little broader than the long radicle, and barely flattish, one would hardly refer the genus to the *Stenolobieæ*, being so unlike the Australian type. It shows that Mr. Bentham was wise in reducing Müller's primary series to the rank of a tribe.



## VI.

## RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

BY WOLCOTT GIBBS, M. D.,

*Rumford Professor in Harvard University.*

(Continued from Vol. XV. p. 21, June, 1879.)

Presented June 25th, 1880.

## PHOSPHO-TUNGSTATES.

THE phospho-tungstates, as already stated, were discovered by Scheibler, who gave provisional formulas for several different compounds. As the German chemist has published nothing farther upon the subject for six years, and as the study of these compounds seemed to be a necessary preliminary to that of other complex inorganic acids, I have devoted much time and labor to them. The investigation has proved very difficult and tedious, but has yielded results which, if not in all cases perfectly definite and conclusive, are yet as I think valuable and interesting. The difficulties met with in the study of this class of salts are in some respects analogous to those which present themselves in the case of the alkaline tungstates. They are mainly as follows:—

1. The normal alkaline phospho-tungstates are readily decomposed by water, yielding acid salts which are often very complex. These acid salts are very slightly soluble, and cannot in general be recrystallized for analysis. They are formed in greater or less proportion whenever we attempt to purify the neutral or less acid salts by recrystallization. In many cases the ratio of tungstic and phosphoric oxides in the neutral salt is changed when the acid salt is formed, so that we can draw no certain conclusion from the constitution of one salt as to that of the other. It is usually very difficult, or even impossible, to pass from the acid back to the primitive normal or neutral salt, because the addition of an alkali produces new compounds.

2. It is difficult by any analytical method which has been devised to determine the percentage of phosphoric oxide with great accuracy,

and very small differences — often not exceeding 0.2% — are sometimes sufficient to change the ratio between the number of atoms of phosphoric and tungstic oxides. In the case of tungstic oxide the divisor which we must employ ( $WO_3 = 232$ ) is so large that a very sensible variation in the percentage of the oxide does not sensibly affect the quotient. It is consequently sometimes difficult to decide between formulas in which, for example, the ratios of the two oxides are as 24 : 1, as 22 : 1, or as 20 : 1.

3. For similar reasons it is very difficult to recognize mixtures of different salts.

4. The alkaline phospho-tungstates are usually efflorescent, — frequently to a remarkable degree.

5. The salts of the different series agree so closely in physical and chemical properties that, as in the case of the tungstates, distinctive tests are not to be found.

6. It is almost impossible to predict what compound will be formed when tungstates and phosphates or phosphoric acid are mixed, even when the mixture is made with the greatest care and in perfectly definite proportions. Very small variations in the conditions of the process materially affect the results.

7. A large proportion of the salts of this series crystallize only from sirupy solutions, and are consequently difficult to purify by recrystallization.

8. When new salts result from a double decomposition the phospho-tungstate formed does not often correspond in composition to that from which it is derived. It may be of a higher or of a lower order.

*Preparation and General Properties.* — Scheibler prepared the salts which he has described by boiling neutral or acid sodic tungstates with half their weight of phosphoric acid. I have found it more convenient to employ the following methods. Solutions of neutral sodic tungstate,  $WO_3Na_2 + 2 aq$ , and of hydro-disodic phosphate,  $PO_4Na_2H + 12 aq$ , in the proportion of  $n$  molecules of the former to  $m$  of the latter, are to be boiled together for some time. The solution has a very strong alkaline reaction. It is to be neutralized with nitric or chlorhydric acid, and then contains the sodium salt — usually acid — of one or another acid of the series. As the sodium salts do not as a rule crystallize as well as those of potassium, I have sometimes found it advantageous to add a solution of potassic bromide or nitrate, when, after some hours, crystals of a potassic salt usually separate in abundance, often in fine colorless and transparent crystals. If a large excess of acid is added at once to the mixed solution of sodic tungstate

and phosphate, an acid sodium salt is often precipitated immediately, and almost always after standing a day or two. But it must be remarked that in this case the proportion of tungstic and phosphoric oxides is not always that which existed in the original mixture. In some cases I have fused the tungstate and phosphate together in definite proportions in a large platinum crucible, but this method does not present any special advantage. In other cases I have dissolved tungstic oxide in solutions of alkaline phosphates. Finally, I have in a few instances employed the original method of Scheibler. The alkaline phospho-tungstates, when not too highly acid, are usually rather easily soluble in water, but in the act of solution they almost always undergo a certain amount of decomposition, a white crystalline powder being formed which is comparatively insoluble. Sometimes the solution becomes milky at once, and remains so for a very long time. In all cases it must be allowed to stand until it becomes perfectly clear, and then poured upon the filter without disturbing the precipitate, as the filtrate would otherwise be turbid.

The alkaline phospho-tungstates are not decomposed by hydric sulphide except to a very limited extent. A current of the gas usually produces a blue color from the reduction of a small portion of the tungstic tetroxide to the lower oxide  $W_2O_5$ . When an alkaline sulphide is added to a solution of a phospho-tungstate a similar reduction is produced. The addition of chlorhydric acid then gives only a small precipitate of tungstic sulphide. Zinc readily reduces a portion of the tetroxide to the blue oxide, but the reduction even after some time is very far from complete. The relations of acid phospho-tungstates to salts of the various alkaloids have already been pointed out by Scheibler. In almost all cases nearly insoluble more or less distinctly crystalline precipitates are formed. I find that a beautiful heavy white crystalline salt is thrown down when an acid phospho-tungstate, as, for example, the sodium salt  $24 WO_3 \cdot P_2O_5 \cdot 2 Na_2O \cdot 4 H_2O$ , is mixed with a solution of urea, or even with urine. In this last case the precipitate contains also slightly soluble salts of potassium and ammonium. It is possible that the reaction may be utilized in animal chemistry. The phospho-tungstates also precipitate egg-albumen as a white flocky substance, which may prove to be a definite salt, in which case the high molecular weight of the acid would be of great value in determining the equivalent of the compound. I have made no experiments in this direction, and throw out the suggestion for what it may be worth.

Mercurous nitrate precipitates all the phospho-tungstates almost

completely. The yellow precipitate formed becomes more dense and compact by boiling with the supernatant liquid. It is nearly insoluble in pure water, but dissolves to some extent even in very dilute nitric acid. Dilute chlorhydric acid decomposes the salt, phospho-tungstic acid being set free. The mercurous salts of the series are the only ones which are sufficiently insoluble to be available in analysis.

Soluble salts of the different series of phospho-tungstates usually possess a strongly marked bitter taste. In a single instance the taste is at once sweet and astringent. The salts which are acid in constitution exhibit a strongly marked acid reaction.

*Analytical Methods.* — To determine the sum of the percentages of tungstic and phosphoric oxides the salt was dissolved in water or dilute nitric acid, and the two oxides precipitated together by means of mercurous nitrate with the addition of mercuric oxide, as in the estimation of tungstic oxide in the alkaline tungstates already described. This method gives good results only when used with great care, as my assistant, Dr. Gooch, observed that the high temperature and long-continued heat required to expel the whole of the mercury also drove off phosphoric oxide, so that the results frequently varied very materially, and were almost always too low. I have sometimes preferred to precipitate the two oxides with mercurous nitrate in small excess from the boiling solution, — as in the case of the tungstates, — and then to evaporate to perfect dryness on a water-bath, continuing the heat until the whole of the free nitric acid was expelled. The dry mass of mercurous phospho-tungstate and basic nitrate adheres somewhat to the evaporating dish, but not so as to render its removal very difficult. Dr. Gooch found that the adhesion was almost entirely prevented by first evaporating the solution and precipitate to a small volume, and then adding water in considerable quantity and evaporating again, this time to perfect dryness. No phosphoric oxide is vaporized on ignition for an hour at a cherry-red heat, and it is not usually necessary to ignite the mixed oxides a second time so as to insure a constant weight, though it is always better to do so. The yellow powder remaining after ignition is a mixture of tungstic oxide,  $\text{WO}_3$ , and phosphoric oxide,  $\text{P}_2\text{O}_5$ , from which water removes a portion, but not the whole, of the latter. The quantitative determination of the sum of the two oxides by this method is very nearly, but not absolutely, accurate. A trace of phosphoric acid almost always remains in the filtrate from the mercurous salt, and may be detected by evaporating this to dryness, expelling the mercurous oxide by heat, and then igniting a portion of the residue with magnesium wire. The

loss of phosphoric oxide is, however, extremely small, and probably never exceeds two or three hundredths of one per cent. The tungstic oxide was always determined by subtracting the phosphoric oxide as directly determined from the sum of the two oxides. My various attempts to determine the two oxides together by precipitation with salts of lead or barium, after neutralization with an alkali, proved failures in all cases.

The precise quantitative separation and estimation of phosphoric oxide in the phospho-tungstates is a matter of no small difficulty. After many trials of various methods, the separation by means of magnesia-mixture was found to give the best results, magnesian chloride being employed. Only, in all cases in which this method is used, it is necessary to redissolve the ammonio-magnesian phosphate first precipitated, and to precipitate the salt a second time with ammonia. The whole subject was specially investigated by Dr. F. A. Gooch, and I shall do him and the process the fullest justice by referring to his paper in Volume XV. of these Proceedings. Since the publication of Dr. Gooch's paper, I have also used in many cases the following process, which gives excellent results. The phosphoric oxide is to be precipitated in the usual manner as ammonio-magnesian phosphate, and well washed with magnesia-mixture and ammonia. The precipitate is to be redissolved in chlorhydric acid, ammonia added in small excess, and afterwards acetic acid, until the reaction is faintly but distinctly acid. The phosphoric oxide is then to be precipitated from the last solution by uranio-sodic acetate in excess. The precipitate must be allowed to settle completely, and the clear supernatant liquid poured upon the filter without disturbing the precipitate. A moderately strong solution of ammoniac nitrate is then to be added, and the precipitate again allowed to settle. After repeating this process two or three times, the precipitate may be brought upon the filter and washed with solution of ammoniac nitrate. In this manner there is no danger of obtaining a turbid or milky filtrate. After drying, the precipitate is to be ignited, moistened if necessary with nitric acid, and again ignited. This process is somewhat longer than that by double precipitation and estimation as magnesian pyrophosphate, but is, I think, rather more accurate. In almost all the analyses, by either method, the filtration and washing of the precipitate was effected by means of the asbestos filters devised by Dr. Gooch.\* It is hardly possible to speak too highly of this admirable contrivance, which in a very large number of

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\* Proceedings of American Academy, Vol. XIII. p. 342.

cases is to be preferred to any other mode of filtering, and which has been in daily use in my laboratory for nearly two years, with scarcely a single instance of failure. In many of the earlier analyses the phosphoric oxide was precipitated as ammonio-magnesian phosphate after the addition of citric acid in quantity about equal to the weight of salt taken. Dr. Gooch's later experiments showed that this method gave results which were about 8% too high when the precipitate — as was always the case — was not redissolved and thrown down a second time. In some cases I have applied this determination as a correction to the direct result of the analysis.

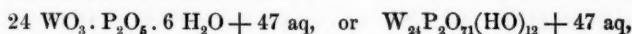
As in the analyses of the alkaline tungstates, I have usually determined the alkali by difference, making direct estimations only in doubtful cases. Ammonia was always expelled by boiling the salt with sodic hydrate, collecting in chlorhydric acid, and weighing as ammoniac chloride. Baric oxide was also sometimes estimated by difference. When precipitated from a solution of baric phospho-tungstate by sulphuric acid, the sulphate always contains phosphoric oxide, and the same is true when ammoniac carbonate and ammonia are employed. Phospho-tungstates which are insoluble in water may be resolved by fusion with an alkaline carbonate, preferably by the mixed carbonates:  $\text{CO}_3$  KNa. Water is best determined from the loss by ignition, but in some cases I have found it best to ignite with a weighed quantity of borax.

*Twenty-four Atom Series. Phospho-tungstic Acid.* — The acid is most conveniently prepared by decomposing mercurous phospho-tungstate by dilute chlorhydric acid. I have found it best to proceed as follows. To the mixture of 24 molecules of normal sodic tungstate and 2 molecules of sodic phosphate in solution, after boiling for some time, dilute nitric acid free from chlorine is to be added until the reaction is quite distinctly acid. The solution is then to be precipitated hot by mercurous nitrate in small excess, and the yellow flocky mercurous salt washed thoroughly by decantation with hot water. Toward the end of the operation a few drops of solution of mercurous nitrate may be added to the water, as the washings are otherwise apt to become milky. After washing, dilute chlorhydric acid is to be added in small quantities at a time until the yellow color disappears, and is replaced by the white of mercurous chloride. It is well to set aside a small quantity of the mercurous phospho-tungstate, and to add this to the solution of the acid so as to insure the separation of any remaining traces of chlorhydric acid. After complete subsidence the supernatant liquid is to be filtered off clear and then evaporated in vacuo over sulphuric acid. The sirupy

faintly violet liquid gives splendid large transparent crystals of phospho-tungstic acid, which are sometimes colorless and sometimes sulphur-yellow. The crystals effloresce with great rapidity, and therefore do not admit of measurement. They appear to be regular octahedra. The solution of the acid is colorless, and has a strongly acid reaction and bitter taste. Of these crystals, —

1.2791 gr. lost on ignition	0.1809 gr. water	= 14.14%
1.3005 gr. lost on ignition with fused borax	0.1842 gr. water	= 14.16%
1.4151 gr. gave	1.2130 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 85.72%
1.5416 gr. gave	1.3201 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 85.64%
1.7365 gr. gave	0.0616 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.26% $\text{P}_2\text{O}_5$

The analyses lead to the formula

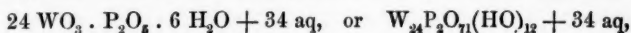


which requires : —

		Cale'd.	Mean.		
24 $\text{WO}_3$	5568	83.55	83.57	83.53	83.61
$\text{P}_2\text{O}_5$	142	2.13	2.11		2.11
53 $\text{H}_2\text{O}$	954	14.32	14.15	14.14	14.16
	6664	100.00	99.83		

As the phosphoric oxide in the analysis was determined after a single precipitation, a correction of 0.15 is applied to the direct result of the analysis. The crystals had slightly effloresced in drying, which explains the deficiency in the water.

A quantity of the 18-atom potassium salt  $18 \text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{K}_2\text{O} + 26 \text{aq}$  was dissolved and precipitated by mercurous nitrate. The mercurous salt was then decomposed by dilute chlorhydric acid, and the solution of phospho-tungstic acid obtained evaporated in a flask at about  $50^\circ \text{C}$ . by means of a water air-pump, and then allowed to stand in a partial vacuum over sulphuric acid. After some days splendid colorless crystals formed, which appeared to be octahedra, but which on standing became columnar in structure, opaque, and yellow. The analyses of these crystals corresponded very closely to the formula



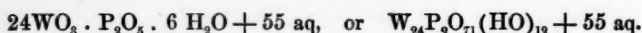
as the following analyses show : —

1.4482 gr. lost on ignition	0.1636 gr. water	= 11.30%
and gave	0.0492 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.17% $\text{P}_2\text{O}_5$
1.5109 gr. lost on ignition	0.1708 gr. water	= 11.31%
and gave	0.0521 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.20% $\text{P}_2\text{O}_5$



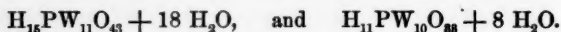
		Cale'd.		
24 WO <sub>3</sub>	5568	86.59	86.50	86.53
P <sub>2</sub> O <sub>5</sub>	142	2.20	2.20	2.17
40 H <sub>2</sub> O	720	11.21	11.30	11.31
	6430	100.00		

The yellow columnar mass, after re-solution and standing over sulphuric acid in pleno gave perfectly colorless regular octahedra, which corresponded to the formula,

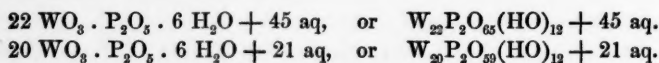


		Cale'd.		
24 WO <sub>3</sub>	5568	81.78	81.75	81.76
P <sub>2</sub> O <sub>5</sub>	142	2.08	2.14	2.15
61 H <sub>2</sub> O	1098	16.14	16.11	16.09
	6808	100.00		

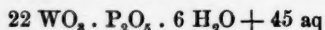
In the cases of the two last-mentioned hydrates of the acid, the phosphoric oxide was determined by two successive precipitations as ammonio-magnesian phosphate. The analyses leave no doubt as to the constitution of the acid. Scheibler obtained two different phospho-tungstic acids, to which he gave respectively the provisional formulas



I should double these and write



I have not obtained the acid of the 20-atom series, though I shall show further on that there is at least one well-defined salt in which the ratio of tungstic to phosphoric oxide is as 20 to 1. Scheibler does not give the method which he employed for the separation of the two oxides, and I consider it at least probable that his acid



is identical with the first of the three hydrates which I have described above.

The solution of phospho-tungstic acid forms a colorless heavy oily liquid, with a high refracting power. It has an acid as well as bitter taste, and readily expels carbonic dioxide from carbonates. On standing for some days, the solution undergoes partial decomposition with deposition of a white crystalline powder. This powder is also almost always deposited, in greater or less quantity, in the preparation of the



acid, but I could not obtain it in a state of purity sufficient for analysis. It may be worth while to note as a possible source of difference, that Scheibler obtained his acids by the decomposition of the corresponding barium salts by dilute sulphuric acid. The method of preparation which I employed is, I think, preferable.

24 : 2 *Acid Sodio Phospho-tungstate*. — When chlorhydric or nitric acid is added in large excess to a solution of normal sodic tungstate, and of hydrodisodic phosphate containing 24 molecules of the former to 2 of the latter, a salt is obtained which is usually colorless when chlorhydric acid is employed, and pale sulphur yellow when nitric acid is used. This salt crystallizes more easily than the other salts of sodium. According to Dr. Gooch, the small granular crystals appear to be either monoclinic or triclinic. They are readily soluble in water, but invariably undergo a slight decomposition in the act of solution, a small quantity of a white crystalline powder being formed which is insoluble, or but slightly soluble. The yellow and the colorless crystals have the same crystalline form and the same reactions. Their constitution is also the same, as the following analyses show : —

## I.

1.4900 gr. lost on ignition	0.1107 gr. water	= 7.43%
1.1100 gr. gave	1.0016 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 90.23%
1.8072 gr. “	0.0679 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.40% $\text{P}_2\text{O}_5$

## II.

0.9913 gr. lost on ignition	0.1809 gr. water	= 7.34%
0.8945 gr. “	0.0658 gr. “	= 7.32%
1.0745 gr. gave	0.9698 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 90.26%
1.1508 gr. “	0.0420 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.33% $\text{P}_2\text{O}_5$

## III.

1.4933 gr. lost on ignition	0.1115 gr. water	= 7.47%
1.3273 gr. gave	1.1969 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 90.18%
1.5424 gr. “	1.3920 gr. “	= 90.25%
1.2990 gr. “	0.0470 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.31% $\text{P}_2\text{O}_5$
1.1503 gr. “	0.0428 gr. “	= 2.38% “

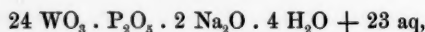
## IV.

1.8027 gr. lost on ignition	0.1349 gr. water	= 7.48%
1.1559 gr. “	0.0860 gr. “	= 7.44%
1.1269 gr. gave	1.0151 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 90.08%
0.9624 gr. “	0.0367 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.44% $\text{P}_2\text{O}_5$
0.6787 gr. “	0.0263 gr. “	= 2.48% “

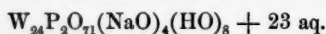
Analyses I. and II. were made with two different preparations of the colorless crystals; III. and IV. were made with the sulphur-yellow salt. The determinations of  $(\text{WO}_3 + \text{P}_2\text{O}_5)$  in I., II., and III. were made by the evaporation process without the use of mercuric oxide, but in IV. the oxide was employed. As a check upon the quantity of sodic oxide two direct determinations were made in III. the oxide being weighed as nitrate. In this manner,

$$\begin{array}{l} 1.3273 \text{ gr. gave } 0.0875 \text{ gr. } \text{NO}_3\text{Na} = 2.40\% \\ 1.2593 \text{ gr. " } 0.0924 \text{ gr. " } = 2.68\% \text{ Na}_2\text{O} \end{array}$$

The mean of these two is 2.54%. As the phosphoric oxide in the analyses above cited was determined from a single precipitation as ammonio-magnesian phosphate, I have, as usual in such cases, applied a correction of 0.15% to the mean. These analyses lead to the formula



or,



		Calc'd.	Mean.						
24 $\text{WO}_3$	5568	88.10	88.04	87.98	88.08	88.02	88.02	88.09	
$\text{P}_2\text{O}_5$	142	2.25	2.24	2.25	2.18	2.16	2.13	2.29	2.33
2 $\text{Na}_2\text{O}$	124	1.97	2.27	...	...	...	...	...	...
27 $\text{H}_2\text{O}$	486	7.68	7.49	7.43	7.32	7.34	7.47	7.50	7.48
		6320	100.00						

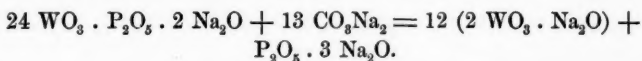
The mean of the five determinations of  $(\text{WO}_3 + \text{P}_2\text{O}_5)$  is 90.20. The formula requires 90.35. There can, I think, be no reasonable doubt as to the constitution of the acid sodium salt, though it is difficult to obtain it in a state of absolute purity. The salt is very conveniently prepared, however, and makes an excellent reagent for alkaloids. For this special purpose it is best to mix the normal tungstate and hydrodisodic phosphate in the proportion of 24 atoms of the former to 3 or 4 of the latter, boil the mixed solutions for a short time, filter, and add chlorhydric acid in excess, but in small successive portions. A precipitate is usually formed on each addition of acid which disappears on stirring the liquid. On standing, a mass of crystals of the acid salt separates. This should be drained, washed with a little cold water, then dissolved in cold water for a reagent, the clear liquid only being used.

The 24 : 2 acid phospho-tungstate of sodium appears to be always formed when an excess of chlorhydric or nitric acid is added to a so-

lution containing sodic tungstate and phosphate, in which the proportion of the latter to that of the former is as 1 to 12, or as 1 to any number less than 12. In other words, it appears to be the limiting term of all the series. When the salt is fused with sodic carbonate, carbonic dioxide is given off, but not in the proportion which might be expected. In one experiment,

$$\begin{array}{rcl} 2.2298 \text{ gr. lost } 0.5408 \text{ gr. CO}_2 \text{ and H}_2\text{O} & = & 16.94\% \\ 1.2621 \text{ gr. lost on simple ignition } 0.0922 \text{ gr. H}_2\text{O} & = & 7.31\% \end{array}$$

The ratio of the  $\text{WO}_3$  in the salt to the  $\text{CO}_2$  expelled is here as 38 : 22, or very nearly as 24 : 13. If the ratio were as 24 : 13, the reaction would be represented by the equation

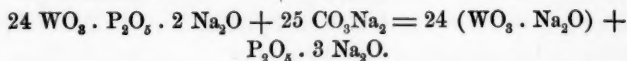


A small proportion of neutral tungstate,  $\text{WO}_4\text{Na}_2$ , is probably formed by the further action of the acid tungstate on the alkaline carbonate.

The 24 : 2 acid sodium salt gives no precipitate with the sulphates of zinc, manganese, and copper; a white crystalline precipitate with argentic nitrate, and after a short time with baric chloride and ammoniac nitrate; no precipitates with calcic and strontic chlorides, but after a short time scanty crystalline salts.

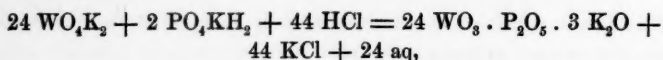
The 24 : 2 acid salt is the only sodium compound of the 24-atom series which I have been able to prepare. When a solution of this salt is carefully neutralized with sodic carbonate, the 6-atom or fully saturated salt,  $24 \text{ WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{ Na}_2\text{O}$ , possibly exists in the solution, but a definite salt could not be obtained by evaporation. When neutral sodic tungstate and hydrodisodic phosphate are mixed in the proportion of 24 : 2, and acetic acid is added to the solution after boiling for some time, no precipitate is formed, but alcohol throws down a colorless oil which soon solidifies to a white gummy mass. I did not obtain a crystalline well-defined salt from this by re-solution and evaporation, but others may perhaps be more successful.

When a sufficient quantity of sodic carbonate is added to a solution of the acid sodic phospho-tungstate, a mixture of sodic tungstate and sodic phosphate appears to be formed.

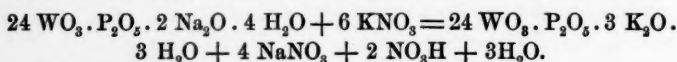


The phospho-tungstate is formed again on adding an excess of acid.

24 : 3 *Acid Potassium Salt*.—When a solution of the 24 : 2 acid sodic salt is added to one of a salt of potassium, a heavy white crystalline very slightly soluble precipitate is formed, either immediately or after a short time. The salt forms very small granular crystals. It requires a large quantity of water for solution, a white much more insoluble salt being formed in small quantity by the action of water, so that the liquid is, and for a long time remains, milky. It is best, therefore, simply to wash the precipitate with cold water until this begins to give a turbid filtrate, and then to dry the salt by pressure with woollen paper. The salt is also formed when chlorhydric or nitric acid is added to a solution of potassic phosphate and tungstate in the proportion of 2 molecules of the former to 24 molecules of the latter, — the two solutions being previously boiled together for some time in a platinum vessel. The reaction in this latter case may be expressed by the equation



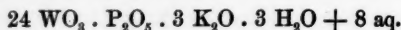
and in the case of precipitation by the acid sodium salt, by the equation



In this salt, —

1.1478 gr. gave	1.0588 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 92.25%
1.1764 gr. “	0.0468 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.54% $\text{P}_2\text{O}_5$
1.7383 gr. lost on ignition	0.0576 gr. water	= 3.31%
1.7638 gr. “ “	0.0578 gr. “	= 3.28%

The analyses lead to the formula

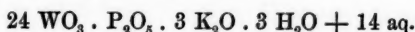


		Calc'd.	Mean.	
24 $\text{WO}_3$	5568	89.93	89.86	89.86
$\text{P}_2\text{O}_5$	142	2.29	2.39	2.39 corrected.
3 $\text{K}_2\text{O}$	283	4.57	4.45	...
11 $\text{H}_2\text{O}$	198	3.19	3.30	3.28 3.31
	6191	100.00	100.00	

n another preparation of the same salt, —

0.7340 gr. gave	0.6660 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 90.74%
1.1400 gr. “	1.0317 gr. “	= 90.50%
0.8028 gr. “	0.0310 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.47% $\text{P}_2\text{O}_5$
1.5568 gr. lost on ignition	0.0805 gr. water	= 5.17%
0.8822 gr. “ “	0.0455 gr. “	= 5.16%

The analyses correspond to the formula



		Calc'd.	Mean.		
24 $\text{WO}_3$	5568	88.38	88.30	88.42	88.18
$\text{P}_2\text{O}_5$	142	2.26	2.32		2.32
3 $\text{K}_2\text{O}$	283	4.49	4.21	...	...
17 $\text{H}_2\text{O}$	306	4.87	5.17	5.16	5.17
	6299	100.00	100.00		

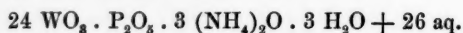
24 : 3 *Acid Ammonium Salt*. — When a solution of a salt of ammonium is mixed with one of sodic tungstate and phosphate, no precipitate is formed, even after standing; but if a large excess of chlorhydric or nitric acid is poured in, a white or very pale yellowish heavy crystalline salt is thrown down in large quantity. This salt is an acid phospho-tungstate of ammonia, the constitution of which varies with the proportions of the salts employed in its preparation and with the conditions of the experiment.

The different salts, however, resemble each other very closely, and may be described in the same terms. They are either perfectly white or have in mass a faint tinge of yellow and an extremely fine-grained crystalline structure. They are very slightly soluble even in hot water, and give milky emulsions which settle very slowly. Like many other phospho-tungstates and tungstates, they are difficult to wash, as they pass through the closest filter-paper with extraordinary facility. This difficulty may, however, be overcome by adding ammonic nitrate to the wash-water. The acid phospho-tungstates of ammonium are soluble in ammonia-water, but the crystals obtained from such solutions are either ammonic tungstates or salts of series different from that to which the salt dissolved belonged. They are readily decomposed by a red heat, leaving a mixture of tungstic and phosphoric oxides. When boiled with mercurous nitrate, they yield mercurous salts and ammonic nitrate.

In one preparation in which sodic tungstate and phosphate were mixed in the proportion of 20 atoms of the former to 2 of the latter, ammonic nitrate was added, and afterward nitric acid. The precipitate was washed with solution of ammonic nitrate, and afterward with alcohol and water, and dried by pressure with woollen paper. Of this salt, —

- 1.3460 gr. lost on ignition 0.1405 gr.  $\text{H}_2\text{O} + \text{NH}_3 = 10.44\%$   
 1.6407 gr. lost on ignition 0.1707 gr.  $\text{H}_2\text{O} + \text{NH}_3 = 10.40\%$   
 1.2038 gr. gave 0.0430 gr.  $\text{P}_2\text{O}_5 \cdot \text{Mg}_2 = 2.27\%$   $\text{P}_2\text{O}_5$  (twice precip.)  
 1.3960 gr. gave 0.0504 gr.  $\text{P}_2\text{O}_5 \cdot \text{Mg}_2 = 2.31\%$  “ “  
 1.4890 gr. gave 0.0720 gr.  $\text{NH}_4\text{Cl} = 2.35\%$   $(\text{NH}_4)_2\text{O}$

These analyses lead to the formula



		Calc'd.	Mean.		
24 $\text{WO}_3$	5568	87.17	87.29	87.27	87.31
$\text{P}_2\text{O}_5$	142	2.22	2.29	2.27	2.31
3 $(\text{NH}_4)_2\text{O}$	156	2.44	2.35		2.35
29 $\text{H}_2\text{O}$	522	8.17	8.07	8.05	8.09
	6388	100.00	100.00		

It will be observed that in this case the 24-atom salt was obtained under conditions which *a priori* should have yielded a 20-atom salt. I have already stated that salts of urea are precipitated from their solutions by acid sodic phospho-tungstate  $24 \text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2 \text{Na}_2\text{O} \cdot 4 \text{H}_2\text{O}$ . The precipitation is, however, not complete, and the process does not appear to be available as a method of analysis.

When phosphate of aniline and 10 : 4 sodic tungstate are dissolved together, and the solution is boiled for a short time, chlorhydric acid gives an abundant yellowish-white precipitate. On re-solution the precipitate yields pale sulphur-yellow crystals, which are readily soluble in alcohol. Phosphate of para-toluidin behaves in a similar manner; the phospho-tungstate formed is readily soluble, and crystallizes in long yellow silky needles.

I did not succeed in making the insolubility of the acid ammonic phospho-tungstate available in analysis, either for the determination of ammonia or for that of phosphoric acid. For the last-named estimation the phospho-molybdates appear to be far better adapted.

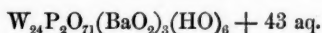
**24 : 3 Acid Barium Salt.** — When 10 : 4 sodic tungstate is dissolved and a small quantity of phosphoric acid is added, the hot solution gives with baric chloride a heavy white flocky precipitate, which readily dissolves in hot dilute chlorhydric acid. The solution, after filtration from a small quantity of flocky matter, is pale yellow, and after some time deposits splendid nearly colorless crystals, which appear to be octahedra. These are readily soluble in hot water without decomposition, and may be repeatedly recrystallized without difficulty. Of these crystals. —

0.7672 gr. gave	0.6278 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 81.83%
1.5557 gr. lost on ignition	0.1872 gr. water	= 12.03%
1.3732 gr. lost on ignition	0.1641 gr. water	= 11.95%
1.6196 gr. gave	0.1547 gr. $\text{SO}_4\text{Ba}$	= 6.27% BaO
and	0.0581 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.29% $\text{P}_2\text{O}_5$
1.2094 gr. gave	0.1158 gr. $\text{SO}_4\text{Ba}$	= 6.28% BaO

The analyses agree fairly well with the formula



or,



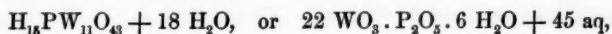
The same salt is formed when two atoms of 12 : 5 sodic tungstate are boiled for a time with two atoms of sodic phosphate and chlorhydric acid is added in excess. Baric chloride then gives after a time crystals exactly similar to those described above. In a salt prepared in this manner, —

1.0020 gr. gave	0.8173 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 81.56%
1.4718 gr. gave	0.1648 gr. $\text{SO}_4\text{Ba}$	= 6.97% BaO
and	0.0518 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.25% $\text{P}_2\text{O}_5$
1.4841 gr. lost on ignition	0.1717 gr. water	= 11.57%

		Calc'd.	Mean.			
24 $\text{WO}_3$	5568	79.57	79.57	79.69		79.46
$\text{P}_2\text{O}_5$	142	2.03	2.12	2.14		2.10
3 BaO	459	6.56	6.62	6.27	6.28	6.97
46 $\text{H}_2\text{O}$	828	11.84	11.78	12.03	11.95	11.57
	6977	100.00	100.09			

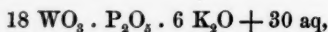
The phosphoric oxide determinations are corrected in both analyses. The percentage of baric oxide as determined by difference, which is the more accurate method, is 6.53. The salt effloresces with extraordinary rapidity, so that it is very difficult to dry it for analysis by pressure between folds of woollen paper.

*Twenty-two Atom Series.* — The phospho-tungstates containing 22 atoms of tungstic oxide to 1 of phosphoric oxide are represented by apparently well-defined salts of potassium, sodium, and ammonium. I have not succeeded in preparing the corresponding acid. As already stated, Scheibler has given provisionally the formula



to an acid which he obtained by the decomposition of a salt of barium, and it may be that this is really the acid of the 22-atom series. Further investigations must decide the point. The salts of the 22-atom series closely resemble those of the 24-atom series already described, and are only to be distinguished from them by analysis.

22 : 2 *Potassium Salt*. — The 18-atom potassium salt,



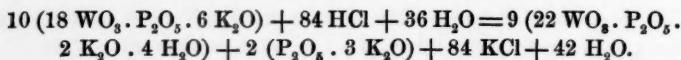
gives with chlorhydric or nitric acid a heavy white fine-granular precipitate of an acid salt which belongs to the 22-atom series, and which has the formula



as the following analyses show : —

1.5679 gr. lost on ignition	0.0318 gr. water	=	2.03%
1.0728 gr. lost on ignition	0.0222 gr. water	=	2.07%
1.5061 gr. gave	1.4250 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	=	94.61%
1.1873 gr. gave	1.1253 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	=	94.78%
2.1607 gr. gave	0.0927 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	=	2.74% $\text{P}_2\text{O}_5$
2.2367 gr. gave	0.0950 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	=	2.72% "
		Calc'd.	Mean.
22 $\text{WO}_3$	5104	92.08	92.11    92.20    92.03
$\text{P}_2\text{O}_5$	142	2.56	2.58    2.59    2.57 corr.
2 $\text{K}_2\text{O}$	189	3.41	3.26    . . .    . . .
6 $\text{H}_2\text{O}$	108	1.95	2.05    2.03    2.07
	<u>5543</u>	<u>100.00</u>	

The salt is very slightly soluble in water. The solution becomes milky, and remains so for a long time. Its formation from the normal 18-atom salt may perhaps be expressed by the equation,

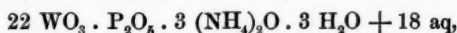


22 : 3 *Ammonium Salt*. — An acid ammonium salt of this series was obtained from a mixture of sodic tungstate and phosphate, to which ammonic nitrate and excess of chlorhydric acid had been added exactly as in the preparation of the 24-atom salt already described. The salt was in very small colorless granular crystals, slightly soluble in cold water, but dissolving to some extent in hot water, giving a milky liquid, settling very slowly. Its other properties are not distinguishable from those of the 24-atom salt. Of this salt,



Gr.	Gr.	Per ct.	Per ct.
0.8697	0.0805	= 9.26 = 90.73	$\text{WO}_3 + \text{P}_2\text{O}_5$
1.5911	0.1470	= 9.24 = 90.76	"
0.9086	0.0837	= 9.21 = 90.79	"
1.0934	0.1009	= 9.21 = 90.79	"
1.0934 gave	0.0439 $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.63 $\text{P}_2\text{O}_5$	
1.7970 "	0.0998 $\text{NH}_4\text{Cl}$	= 2.68 $(\text{NH}_4)_2\text{O}$	

These analyses correspond very closely to the formula,



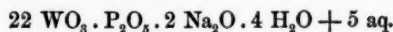
which requires:—

		Calc'd.	Mean.				
22 $\text{WO}_3$	5104	88.30	88.29	88.25	88.28	88.31	88.31
$\text{P}_2\text{O}_5$	142	2.46	2.48	2.48 corr.	...	...	...
3 $(\text{NH}_4)_2\text{O}$	156	2.69	2.68	2.68	...	...	...
21 $\text{H}_2\text{O}$	378	6.55	6.60	6.58	6.56	6.53	6.53
	5780	100.00	100.05				

22 : 2 *Sodium Salt*.—It has already been mentioned that, in the preparation of the acid sodium salt of the 24-atom series, a white very slightly soluble crystalline powder is formed in greater or less quantity. This salt cannot be recrystallized for analysis, and must therefore be washed with cold water to remove traces of the soluble acid salt. Hot water dissolves it in small proportion only, the solution remaining milky for a long time. In one preparation of this salt,—

{ 0.8405 gr. gave 0.7962 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$ = 94.73%	
{ 0.8405 gr. " 0.0330 gr. $\text{P}_2\text{O}_{17}\text{Mg}_2$ = 2.51%	{ twice pre- cipitated { $\text{P}_2\text{O}_5$
1.4990 gr. lost on ignition 0.0403 gr. water = 2.69%	

These analyses lead to the formula



		Calc'd.	
22 $\text{WO}_3$	5104	92.26	92.22
$\text{P}_2\text{O}_5$	142	2.56	2.51
2 $\text{Na}_2\text{O}$	124	2.25	2.58
9 $\text{H}_2\text{O}$	162	2.93	2.69
	5532	100.00	

22 : 4 *Barium Salt*.—This salt was obtained by mixing neutral sodic tungstate and hydro-disodic phosphate in the proportion of 24 : 2, neutralizing with acetic acid, and adding a solution of baric chloride. Small sharp prismatic crystals formed after a short time, soluble in hot

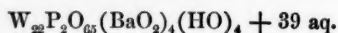
water apparently without any decomposition, and separating again from the solution in colorless needles. Of this salt, —

{ 0.6900 gr. gave	0.5494 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 79.62%
{ 0.6900 gr. "	0.0826 gr. $\text{P}_2\text{O}_{11}\text{U}_2$	= 2.34% $\text{P}_2\text{O}_5$
0.6734 gr. "	0.5372 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 79.71%
1.5296 gr. "	0.2163 gr. $\text{SO}_4\text{Ba}$	= 9.24% BaO
0.9682 gr. lost on ignition	0.1076 gr. water	= 11.12%
0.7064 gr. "	" " 0.0787 gr. "	= 11.14%

These analyses lead to the formula



or,



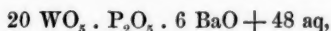
		Calc'd.	Mean.		
22 $\text{WO}_3$	5104	77.37	77.33	77.37	77.28
$\text{P}_2\text{O}_5$	142	2.15	2.34		2.34
4 BaO	612	9.28	9.24		9.24
41 $\text{H}_2\text{O}$	738	11.19	11.13	11.12	11.14
	6596	100.00	100.04		

The phosphoric oxide was precipitated twice.

*Twenty Atom Series.*—The salts of this series closely resemble those which have been described. I did not succeed in preparing the acid, though I made repeated attempts to do so by mixing sodic tungstate and phosphate together in the proportion of 20 molecules of the former to 2 of the latter, neutralizing with nitric acid, precipitating by mercurous nitrate, and decomposing the mercurous salt by dilute chlorhydric acid. The acid formed always underwent partial decomposition upon concentration, a white crystalline powder being separated while the 24-atom acid was formed. The only well-defined salt of the series which I have obtained is the normal barium compound. From this it will doubtless be possible to obtain others by double decomposition.

*Normal 20-atom Barium Salt.*—As the baric phospho-tungstates crystallize in general much more readily than the corresponding sodic salts, I employed them to determine what compounds are formed when sodic tungstate and phosphate are mixed in various proportions. To solutions of the two salts in the ratios of 24 molecules of the former to 2 of the latter, of 18 to 2, and of 12 to 2, chlorhydric acid was added until the reaction became just distinctly acid. Baric chloride was then added in excess, and the solutions were quickly filtered from the insoluble white precipitate formed. Beautiful colorless crystals

formed, which were readily soluble in hot water, and could be recrystallized without difficulty. These salts proved to have in all cases the same composition, and are represented by the formula



as the following analyses show:—

## I.

1.1103 gr. lost on ignition with fused borax	0.1458 gr. = 13.14% water.
1.1831 gr. “ “ “ “	0.1560 gr. = 13.18% “
1.0691 gr. gave	0.7775 gr. $\text{WO}_3$ and $\text{P}_2\text{O}_5$ = 72.72%
0.9390 gr. “	0.6850 gr. “ = 72.84%

## II.

1.0676 gr. lost on ignition	0.1400 gr. = 13.11% water.
0.6550 gr. gave	0.4763 gr. $\text{WO}_3$ and $\text{P}_2\text{O}_5$ = 72.72%

## III.

1.1110 gr. lost on ignition	0.1461 gr. = 13.15% water.
0.6409 gr. gave	0.4667 gr. $\text{WO}_3$ and $\text{P}_2\text{O}_5$ = 72.81%
and	0.0704 gr. $\text{P}_2\text{O}_{11}\text{U}_2$ = 2.18% $\text{P}_2\text{O}_5$
0.6222 gr. gave	0.0710 gr. $\text{P}_2\text{O}_{11}\text{U}_2$ = 2.26% “

Analyses I. were made with the salt from the 24 to 2; II. from that obtained from the 12 to 2; and III. from the salt of the 18 to 2 mixture. The phosphoric oxide was precipitated twice.

		Calc'd.	Mean.					
20 $\text{WO}_3$	4640	70.67	70.55	70.50	70.62	70.50	70.59	
$\text{P}_2\text{O}_5$	142	2.17	2.22	...	...	...	2.18	2.26
6 BaO	918	13.99	14.09	...	...	...	...	
48 $\text{H}_2\text{O}$	864	13.17	13.14	13.14	13.18	13.11	13.15	
	6564	100.00	100.00					

The salt dissolves readily in hot water, giving a somewhat milky solution. Chlorhydric acid gives no precipitate at first, but after a time a white crystalline powder is formed, which is the acid salt of the 24-atom series already described.

The fact that the same salt is formed independently of the proportions of sodic tungstate and phosphate is an important one, and illustrates the peculiarities of the series of phospho-tungstates which I have already pointed out.

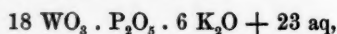
*Eighteen Atom Series.*—When normal sodic tungstate and hydrodisodic phosphate are dissolved together in the proportion of 20 molecules of the former to 2 of the latter, and acetic acid is added to

the boiling solution until a distinctly acid reaction is obtained, alcohol in excess precipitates a white indistinctly crystalline salt. This dissolves very readily in water, but gives on evaporation a gummy mass, and distinct crystals cannot be obtained. The solution of this salt gives no precipitate at first with salts of potassium, but after a short time beautiful colorless crystals are formed in abundance. The salt dissolves in a rather large excess of water, leaving a small quantity of a white insoluble compound. It crystallizes best from a solution which is not very concentrated, and which is allowed to evaporate spontaneously in the air. The crystals obtained in this way are colorless and well-defined prisms. On re-solution it almost always leaves a small quantity of the slightly soluble salt; but when the whole is dissolved together, the more soluble compound crystallizes without perceptible admixture of the other. From very concentrated solutions I obtained a white granular salt, which, on re-solution in a rather large quantity of water, gave the colorless crystals again.

Of the colorless transparent crystals, —

1.1470 gr.	gave 0.9372 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 81.71%
1.5149 gr.	" 1.2387 gr. "	= 81.77%
1.3494 gr.	lost 0.1089 gr. water	= 8.07%
1.5806 gr.	" 0.1277 gr. "	= 8.08%
1.1391 gr.	gave 0.0498 gr. $\text{Mg}_2\text{P}_2\text{O}_7$	= 2.80% $\text{P}_2\text{O}_5$
1.1856 gr.	" 0.0506 gr. "	= 2.93% "
1.5149 gr.	" 0.4738 gr. $\text{AgCl}$	= 10.26% potassium.

These analyses correspond to the formula



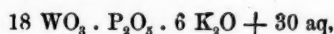
which requires: —

		Calc'd.	Mean.		
18 $\text{WO}_3$	4176	78.81	79.12	78.95	79.01
$\text{P}_2\text{O}_5$	142	2.68	2.62	2.65	2.58
6 $\text{K}_2\text{O}$	566.4	10.69	10.24		
31 $\text{H}_2\text{O}$	414	7.82	8.08	8.07	8.08
	5298.4	100.00			

Of the white granular hydrate, —

1.3868 gr.	gave	1.0985 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 79.21%
0.9528 gr.	"	0.7556 gr. "	= 79.30%
1.0396 gr.	"	0.0409 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 2.57% $\text{P}_2\text{O}_5$
1.0614 gr.	"	0.0425 gr. "	= 2.56% "
1.0102 gr.	lost on ignition	0.1009 gr. water	= 9.99%
1.7974 gr.	" "	0.1800 gr. "	= 10.01%

The corresponding formula is



which requires —

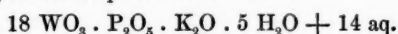
		Calc'd.	Mean.		
18 $\text{WO}_3$	4176	76.98	76.84	76.89	76.80
$\text{P}_2\text{O}_5$	142	2.62	2.42	2.41	2.42
6 $\text{K}_2\text{O}$	566.4	10.44	10.74	...	...
30 $\text{H}_2\text{O}$	540	9.96	10.00	9.99	10.01
	<u>5424.4</u>	<u>100.00</u>			

The prismatic and granular salts, therefore, only differ in water of crystallization. It must be remarked, however, that the corrected percentages of the phosphoric oxide in the analyses of the granular salt are too low, which is unusual.

18 : 1 *Acid Potassium Salt*. — When the normal salt is dissolved in water and chlorhydric acid is added in excess, a white crystalline precipitate is formed, which is but very sparingly soluble in water. Of this salt, —

1.2955 gr. gave	1.1828 gr. $\text{WO}_3 + \text{P}_2\text{O}_5 =$	91.30%
1.3200 gr. “	1.1994 gr. “	= 90.86%
1.1390 gr. “	0.0592 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 3.32% $\text{P}_2\text{O}_5$
1.5900 gr. “	0.0817 gr. “	= 3.29% “
1.5225 gr. lost on ignition	0.1087 gr. water	= 7.14%
1.1966 gr. “ “	0.0856 gr. “	= 7.16%

These analyses correspond to the formula



		Calc'd.	Mean.		
18 $\text{WO}_3$	4176	87.84	87.93	88.15	87.71
$\text{P}_2\text{O}_5$	142	2.99	3.15	3.17	3.14 corrected.
$\text{K}_2\text{O}$	94.4	1.98	1.77	...	...
19 $\text{H}_2\text{O}$	342	7.19	7.15	7.16	7.14
	<u>4754.4</u>	<u>100.00</u>	<u>100.00</u>		

*Ammonium Salt*. — The ammonium salt of the 18 atom series may be prepared in the manner given above for the normal potassic compound. When ammoniac acetate and alcohol are mixed with a concentrated solution of the sodium salt, no precipitate is formed at first, but after some hours a mass of white crystals is thrown down. After washing with alcohol and re-solution, crystals may sometimes be obtained, but the salt usually forms a nearly colorless gummy mass. In this case white opaque crystals separate from a thick and sirupy

mother liquor. The crystals are soft and gummy to the touch. I did not succeed in obtaining the salt in a state of purity suitable for analysis.

*Sixteen Atom Series.* — The only representatives of this series which I have obtained are salts of calcium, potassium, and ammonium. They are all well defined and more or less distinctly crystalline.

16 : 1 *Acid Calcium Salt.* — When calcic tungstate,  $\text{WO}_4\text{Ca}$ , is boiled with a pure dilute solution of phosphoric acid, the salt is dissolved very slowly; but on addition of a few drops of chlorhydric acid, the tungstate passes quickly into solution. The liquid deposits on evaporation colorless flat tabular crystals readily soluble in water. Of these crystals, —

{ 0.7356 gr. gave	0.6992 gr. $\text{WO}_3 + \text{P}_2\text{O}_5 = 95.05\%$
{ 0.7356 gr. “	0.0390 gr. $\text{P}_2\text{O}_7\text{Mg}_2 = 3.39\% \text{P}_2\text{O}_5$
1.0347 gr. lost on ignition	0.0366 gr. water = 3.54%

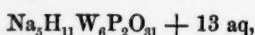
The phosphoric acid was twice precipitated. The analyses lead to the formula



which requires : —

		Calc'd.	
16 $\text{WO}_3$	3712	91.56	91.66
$\text{P}_2\text{O}_5$	142	3.50	3.39
$\text{CaO}$	56	1.38	1.41 (diff)
8 $\text{H}_2\text{O}$	144	3.56	3.54
	4054	100.00	

16 : 4 *Acid Potassium Salt.* — In the attempt to prepare the sodium salt to which Scheibler gave provisionally the formula



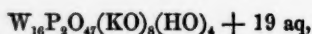
I obtained a thick sirupy liquid, which on dilution with water gave with potassic bromide, after standing a few hours, beautiful colorless needles. The salt is readily soluble in hot water. After recrystallization, —

0.5991 gr. gave	0.5000 gr. $\text{WO}_3 + \text{P}_2\text{O}_5 = 83.46\%$
2.1547 gr. “	0.1005 gr. $\text{P}_2\text{O}_7\text{Mg}_2 = 2.98\% \text{P}_2\text{O}_5$
1.0492 gr. lost on ignition	0.0841 gr. water = 8.01%

The analyses give the formula



or,



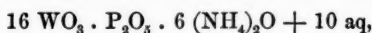
which requires : —

		Calc'd.	
16 WO <sub>3</sub>	3712	80.53	80.48
P <sub>2</sub> O <sub>5</sub>	142	3.08	2.98
4 K <sub>2</sub> O	377.6	8.19	8.53 (diff.)
21 H <sub>2</sub> O	378	8.20	8.01
	4609.6	100.00	

16:6 *Ammonium Salt*. — This beautiful salt was prepared by adding a solution of ammoniac chloride to the sirupy liquid obtained by boiling 12:5 sodic tungstate with half its weight of a strong solution of pure phosphoric acid. After standing twelve hours an abundant precipitate of the ammonium salt was formed. This precipitate, after being well drained and twice recrystallized, gave very fine flat prismatic crystals. It is the best-defined ammonium salt which I have obtained. The salt is readily soluble in hot water, and crystallizes as the solution cools. Of this salt, —

1.4108 gr. lost on ignition	0.1627 gr. H <sub>2</sub> O + NH <sub>3</sub>	= 11.58%
{ 0.7705 gr. " "	0.0886 gr. " "	= 11.49%
0.7705 gr. gave	0.1243 gr. P <sub>2</sub> O <sub>5</sub> U <sub>2</sub>	= 3.21% P <sub>2</sub> O <sub>5</sub>
0.9629 gr. " "	0.1430 gr. NH <sub>4</sub> Cl	= 7.17% (NH <sub>4</sub> ) <sub>2</sub> O

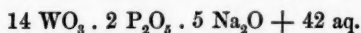
The analyses correspond with the formula



which requires : —

		Calc'd.	Mean.		
16 WO <sub>3</sub>	3712	85.41	85.28	85.30	85.26
P <sub>2</sub> O <sub>5</sub>	142	3.27	3.21		3.21
6 (NH <sub>4</sub> ) <sub>2</sub> O	312	7.18	7.17		7.17
10 H <sub>2</sub> O	180	4.14	4.34	4.32	4.36
	4346	100.00	100.00		

*Fourteen to Two Series*. — The only compound of this series which I have obtained is a sodium salt with the empirical formula



I regard this as a double salt, or perhaps as a compound of an 8-atom and a 6-atom salt.

14 : 5 *Sodium Salt*. — In the communication already referred to,\* Scheibler described briefly a sodium salt to which he gave provisionally the formula




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\* Berichte der Deutschen Chemischen Gesellschaft, V. 801.

This salt was obtained by boiling 12 : 5 sodic tungstate with half its weight of phosphoric acid. After a short time the salt separates in beautiful crystals. As Scheibler's salt evidently belongs to a 6-atom series, and has therefore a special theoretical interest, I endeavored in various ways to prepare it, but in all cases without success. By boiling 12 : 5 sodic tungstate with half its weight of phosphoric acid I obtained a thick sirupy liquid, which after long standing gave crystals. In another experiment about 75 gr. of the sodium salt were boiled with 13 gr. of sirupy pure phosphoric acid. After dilution and standing for some days, splendid colorless prismatic crystals separated, identical in appearance with those of the last experiment. These were redissolved and recrystallized several times. Of this salt, —

0.5551 gr. gave	0.4272 gr. $\text{WO}_3 + \text{P}_2\text{O}_5 =$	76.95%
0.5787 gr. “	0.4459 gr. “	= 77.06%
1.5430 gr. “	1.1884 gr. “	= 77.02%
1.0058 gr. “	0.0980 gr. $\text{P}_2\text{O}_5, \text{Mg}_2$	= 6.35% $\text{P}_2\text{O}_5$
1.0285 gr. “	0.1014 gr. “	= 6.34% “
1.0023 gr. “	0.3214 gr. $\text{P}_2\text{O}_{11}\text{U}_2$	= 6.38% “
1.0152 gr. lost on ignition	0.1656 gr. water	= 16.31%
1.0240 gr. “ “	0.1677 gr. “	= 16.37%
0.9922 gr. “ “	0.1612 gr. “	= 16.24%

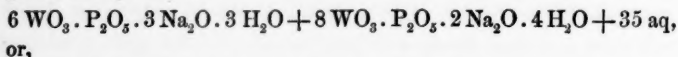
These analyses correspond fairly well to the formula



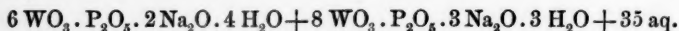
which requires : —

		Calc'd.	Mean.			
14 $\text{WO}_3$	3248	70.64	70.65	70.59	70.70	70.66
2 $\text{P}_2\text{O}_5$	284	6.18	6.36	6.35	6.34	6.38
5 $\text{Na}_2\text{O}$	310	6.74	6.65	...	...	...
42 $\text{H}_2\text{O}$	756	16.44	16.34	16.31	16.37	16.34
	4598	100.00				

The phosphoric oxide, which was twice precipitated, is too high, but it may be that in such salts a third precipitation is necessary to effect a perfect separation. I should write the formula of the salt, provisionally, either,



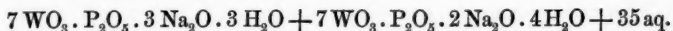
or,



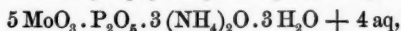
There appears to be no reason for distributing the sodic oxide in one way rather than in the other. On the other hand, it is perhaps equally



probable that the salt is a compound of two acid salts of a 7-atom series, and that its formula is



Among the corresponding phospho-molybdates there is at least one series in which the number of atoms of the teroxide is odd. Potassium and ammonium salts in this series have respectively the formulas

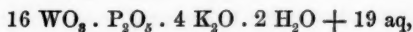


if, provisionally, we consider the acid as 12-basic. With respect to the formula given above, and which is that of an acid double salt, I may remark that I shall describe farther on a salt of the 5-atom molybdenum series with the formula

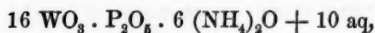


and that Rammelsberg has already described the corresponding potassium compound. From the general analogy between tungsten and molybdenum, the existence of phospho-tungstates with an uneven number of atoms of tungstic oxide may be fairly inferred from that of phospho-molybdates of the type of the 5-atom compounds above mentioned. I must leave the question undecided, for the present at least, as I have not succeeded in obtaining corresponding salts of potassium, ammonium, strontium, or calcium.

The salt crystallizes in long, flat prismatic forms, and appears to be perfectly homogeneous, so that I believe it should be regarded as a definite compound, and not as a mixture. It is very soluble in water, and crystallizes only from sirupy solutions. It has a strongly marked sweet taste, which is at the same time astringent and very slightly bitter. The solution of the sodium salt gives with potassic bromide a beautiful crystalline precipitate, already described, and having the formula



and with ammoniac chloride, the ammonium salt



also noticed above.

I endeavored to obtain the normal 6-atom sodium salt  $6 \text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{Na}_2\text{O}$  by boiling six atoms of neutral sodic tungstate with

the calculated quantity of pure phosphoric acid, but the experiment was unsuccessful.

When a solution of hydro-disodic phosphate is heated, and freshly prepared tungstic oxide is added, in small portions at a time, the oxide is readily dissolved with formation of a colorless or faintly bluish liquid. The solution gave crystalline precipitates with baric chloride and argentic nitrate, but the salts formed proved on analysis to be only mixtures. An ammonium salt was prepared by adding ammoniac nitrate and nitric acid to the solution of the sodium salt. The ratio of tungstic to phosphoric oxide in the white crystalline salt formed was as 20 : 1 very closely; but this does not lead to any inference as to the formula of the sodium salt in solution. Tribasic sodic phosphate also dissolves tungstic oxide readily, and the same is true as regards ammoniac phosphate; but I could not obtain definite salts from either solution. Potassic phosphate dissolves tungstic oxide very slowly, and only by long boiling. No definite compound was formed in this case.

When hydro-disodic phosphate and tungstic oxide are fused together the latter dissolves and forms a colorless fused mass. This is soluble in water, but, as in the other cases, gives no single well defined salt. I have made no experiment to determine whether phospho-tungstates of the lower orders dissolve freshly precipitated tungstic oxide so as to form the higher terms in the series. The extraordinary amount of time and labor which I have already spent upon the subject must be my excuse for leaving this and many other interesting points to other investigators. There is no part of the subject which will not amply repay a new and careful study.

#### ARSENIO-TUNGSTATES.

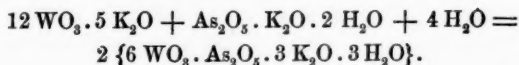
When solutions of alkaline tungstates and arsenates are mixed it frequently happens that white crystalline precipitates are formed, the supernatant liquid becoming strongly alkaline. These precipitates are arsenio-tungstates, and, as might be expected, correspond in a general way to the class of phospho-tungstates already described. They appear to be as a rule less well defined than these last, and, so far as I have been able to discover, exhibit no character of special interest. In analyzing the few salts of this series which I have studied, I have employed the same methods which I have used for the analysis of the phospho-tungstates. Only the conditions are necessarily in some respects different. Arsenic and tungstic oxides were precipitated together

by mercurous nitrate, mercuric oxide being employed to secure perfect neutrality. The mercurous salt was then separated upon an asbestos filter, and, after drying, ignited — finally with the blast-lamp — until a constant weight was obtained. In this manner very nearly the whole of the arsenic oxide was volatilized. There is no danger of a reduction to metallic arsenic if the crucible containing the asbestos and precipitate is placed within another, covered, and then cautiously heated. The arsenic oxide is best determined as ammonio-magnesian arsenate, using a large excess of magnesia-mixture in the first precipitation. Two precipitations are necessary to secure a perfect separation; the salt is to be collected on an asbestos filter, and dried in the usual manner. In determining water, or water and ammonia, in these salts, it is best to ignite with a weighed quantity of fused sodic tungstate, as suggested to me by Dr. Gooch; only it must be observed that the fused tungstate is rather deliquescent. With all these precautions fairly good results may be obtained. I endeavored to separate arsenic from tungstic oxide by boiling the salt with dilute phosphoric acid, reducing the arsenic to arsenous acid by sulphurous acid, and then precipitating by sulphydric acid as  $\text{As}_2\text{S}_3$ . This method appears to give a complete separation, but is very tedious and circumstantial.

*Acid 3-atom Potassic Arsenio-tungstate.* — When 12 : 5 acid potassic tungstate is dissolved, and a solution of potassic arsenate,  $\text{AsO}_4\text{KH}_2$ , is added, a white very fine-grained precipitate is formed. When an excess of the arsenate is employed, and the mixed solutions are evaporated upon a water-bath, a perfectly white insoluble salt is separated, which is the acid arsenio-tungstate



The formation of this salt may be represented by the equation



For analysis the salt was washed upon a filter with hot water, then dried upon paper, and afterward — as the mass remained pasty — upon a water-bath, where it finally dried to a hard white mass. Of this salt, —

0.8276 gr. gave 0.5902 gr. $\text{WO}_3$	= 71.31%
0.7197 gr. “ 0.5130 gr. “	= 71.28%
1.9815 gr. “ 0.3841 gr. $\text{As}_2\text{O}_5\text{Mg}_2(\text{MH}_4)_2 + \text{H}_2\text{O}$	= 11.73% $\text{As}_2\text{O}_5$
1.3507 gr. lost on ignition 0.0357 gr. water	= 2.64%

The formula requires :—

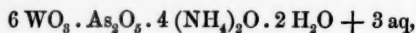
		Calc'd.	
6 $\text{WO}_3$	1392	71.05	71.31
$\text{As}_2\text{O}_5$	230	11.75	11.73
3 $\text{K}_2\text{O}$	283	14.45	14.33 (diff.)
3 $\text{H}_2\text{O}$	54	2.75	2.64
	<u>1959</u>	<u>100.00</u>	

The salt dissolves readily in alkaline hydrates. Its chief interest lies in the fact that it serves to establish the existence of a 6-atom series of arsenio-tungstates.

*Acid 6 : 4 Ammonium Salt.*—When ammonic arsenate  $\text{AsO}_4\text{NH}_4$  and neutral sodic tungstate are dissolved together, no precipitate is formed at first, but after a short time a dense white crystalline salt is thrown down, which after twelve hours becomes abundant. Boiling water dissolves this salt readily, but it does not crystallize well from the solution, forming only a thick white mass. If this mass be dissolved in water, nitric acid added in excess gives a white crystalline precipitate, but slightly soluble in the acid liquid and in water. Of this salt, after washing with cold water, —

0.8255 gr. gave 0.6013 gr. $\text{WO}_3$	= 72.84%
1.9486 gr. " 0.3980 gr. $\text{As}_2\text{O}_5 \cdot \text{Mg}_2(\text{NH}_4)_2 + \text{H}_2\text{O}$	= 12.36% $\text{As}_2\text{O}_5$
1.2494 gr. " 0.2635 gr. $\text{NH}_4\text{Cl}$	= 10.25%

The analyses agree — though not very closely — with the formula



which requires :—

		Calc'd.	
6 $\text{WO}_3$	1392	72.50	72.84
$\text{As}_2\text{O}_5$	230	11.98	12.36
4 $(\text{NH}_4)_2\text{O}$	208	10.83	10.25
5 $\text{H}_2\text{O}$	90	4.69	4.55 (diff.)
	<u>1920</u>	<u>100.00</u>	

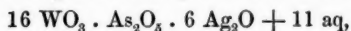
The differences are, I think, not greater than may be expected in cases in which the salt analyzed cannot be purified by recrystallization.

*Normal 16 : 6 Silver Salt.*—I obtained this salt by the following process : 100 gr. neutral sodic tungstate and 25 gr. arsenic acid were dissolved together and the solution boiled for some time, then filtered and evaporated upon a water-bath. After a day much sodic arsenate separated in crystals. The filtrate from these crystals deposited a

white indistinctly crystalline mass. This was redissolved and potassic bromide added in excess, when an abundant white crystalline fine-grained precipitate was thrown down, which was drained on the filter-pump, and then washed with cold water. This was dissolved in much boiling water, and argentic nitrate added, when a white crystalline salt was thrown down mixed with brownish-red crystals of argentic arsenate. The mass was treated with very dilute nitric acid, which readily dissolved the arsenate, the undissolved portion appearing under a lens as made up of opaque white acicular crystals. These were well drained, washed with cold water, and dried on paper by pressure, when the mass showed a faint yellowish tint. The salt is but slightly soluble in cold water. Of this salt, —

0.7488 gr. gave	0.5024 gr. $\text{WO}_3$ = 67.09%
0.7531 gr. “	0.5067 gr. “ = 67.29%
2.0321 gr. “	0.6147 gr. $\text{AgCl}$ = 24.45% $\text{Ag}_2\text{O}$
1.0215 gr. “	0.3096 gr. “ = 24.48% “
0.9209 gr. lost on ignition	0.0340 gr. water = 3.69%

The analyses correspond tolerably well to the formula



which requires: —

		Calc'd.		
16 $\text{WO}_3$	3712	67.10	67.09	67.29
$\text{As}_2\text{O}_5$	230	4.16	4.65	(diff.)
6 $\text{Ag}_2\text{O}$	1392	25.16	24.45	24.48
11 $\text{H}_2\text{O}$	198	3.58	3.69	
	<u>5532</u>	<u>100.00</u>		

I do not place implicit confidence in the formula given, as the two determinations of argentic oxide are too low. It is very possible that the salt was slightly decomposed by the dilute nitric acid employed to remove the arsenate. But in any case it is proved that arsenio-tungstates exist in which the ratio of  $\text{WO}_3$  to  $\text{As}_2\text{O}_5$  is higher than 6 : 1, and a method of obtaining such compounds is pointed out.

*General Conclusions.* — The general results of my investigation of the phospho-tungstates may be stated briefly as follows: —

1. The phospho-tungstates form a series of which the lowest term probably contains six atoms of tungstic to one of phosphoric oxide, and the highest, twenty-four atoms of tungstic to one of phosphoric oxide.

2. At least the greater number of phospho-tungstates contain an even number of atoms of tungstic oxide. The homologizing term for these cases is therefore  $2 \text{WO}_3$ .

3. The highest number of atoms of base observed in any case is six (old style), which implies that each acid contains twelve atoms of hydroxyl.

4. In all cases observed the number of atoms of hydroxyl replaced by a monatomic metal is even.

5. One instance occurs in which two acid phospho-tungstates of different orders appear to unite to form a definite compound; but this case admits of a different explanation.

6. In all phospho-tungstates studied the number of atoms of base or of hydroxyl is more than sufficient to saturate the phosphoric oxide present, if we admit that the acid is 12-basic. At least a part of the hydroxyl or base must therefore be united to tungstic oxide.

For greater facility of comparison I have brought together the formulas of all the compounds described in this paper, writing them both with the old and the new notation.

24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{H}_2\text{O} + 47 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{HO})_{12} + 47 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{H}_2\text{O} + 34 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{HO})_{12} + 34 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{H}_2\text{O} + 55 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{HO})_{12} + 55 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2 \text{Na}_2\text{O} \cdot 4 \text{H}_2\text{O} + 23 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{NaO})_4(\text{HO})_8 + 23 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 \text{K}_2\text{O} \cdot 3 \text{H}_2\text{O} + 8 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{KO})_6(\text{HO})_6 + 8 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 \text{K}_2\text{O} \cdot 3 \text{H}_2\text{O} + 14 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{KO})_6(\text{HO})_6 + 14 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3(\text{NH}_4)_2\text{O} \cdot 3 \text{H}_2\text{O} + 26 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{NH}_4\text{O})_6(\text{HO})_6 + 26 \text{ aq}$
24 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 \text{BaO} \cdot 3 \text{H}_2\text{O} + 43 \text{ aq}$	$\text{W}_{24}\text{P}_2\text{O}_{71}(\text{BaO})_3(\text{HO})_6 + 43 \text{ aq}$
22 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2 \text{K}_2\text{O} \cdot 4 \text{H}_2\text{O} + 2 \text{ aq}$	$\text{W}_{22}\text{P}_2\text{O}_{65}(\text{KO})_4(\text{HO})_8 + 2 \text{ aq}$
22 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3(\text{NH}_4)_2\text{O} \cdot 3 \text{H}_2\text{O} + 18 \text{ aq}$	$\text{W}_{22}\text{P}_2\text{O}_{65}(\text{NH}_4\text{O})_6(\text{HO})_6 + 18 \text{ aq}$
22 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2 \text{Na}_2\text{O} \cdot 4 \text{H}_2\text{O} + 5 \text{ aq}$	$\text{W}_{22}\text{P}_2\text{O}_{65}(\text{NaO})_4(\text{HO})_8 + 5 \text{ aq}$
22 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 4 \text{BaO} \cdot 2 \text{H}_2\text{O} + 39 \text{ aq}$	$\text{W}_{22}\text{P}_2\text{O}_{65}(\text{BaO})_4(\text{HO})_4 + 39 \text{ aq}$
20 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{BaO} + 48 \text{ aq}$	$\text{W}_{20}\text{P}_2\text{O}_{59}(\text{BaO})_6 + 48 \text{ aq}$
18 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{K}_2\text{O} + 23 \text{ aq}$	$\text{W}_{18}\text{P}_2\text{O}_{53}(\text{KO})_{12} + 23 \text{ aq}$
18 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6 \text{K}_2\text{O} + 30 \text{ aq}$	$\text{W}_{18}\text{P}_2\text{O}_{53}(\text{KO})_{12} + 30 \text{ aq}$
18 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{K}_2\text{O} \cdot 5 \text{H}_2\text{O} + 14 \text{ aq}$	$\text{W}_{18}\text{P}_2\text{O}_{53}(\text{KO})_2(\text{HO})_{10} + 14 \text{ aq}$
16 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{CaO} \cdot 5 \text{H}_2\text{O} + 3 \text{ aq}$	$\text{W}_{16}\text{P}_2\text{O}_{47}(\text{CaO})_2(\text{HO})_{10} + 3 \text{ aq}$
16 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 4 \text{K}_2\text{O} \cdot 2 \text{H}_2\text{O} + 19 \text{ aq}$	$\text{W}_{16}\text{P}_2\text{O}_{47}(\text{KO})_8(\text{HO})_4 + 19 \text{ aq}$
16 $\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6(\text{NH}_4)_2\text{O} + 10 \text{ aq}$	$\text{W}_{16}\text{P}_2\text{O}_{47}(\text{NH}_4\text{O})_{12} + 10 \text{ aq}$
14 $\text{WO}_3 \cdot 2 \text{P}_2\text{O}_5 \cdot 5 \text{Na}_2\text{O} + 42 \text{ aq}$	
6 $\text{WO}_3 \cdot \text{As}_2\text{O}_5 \cdot 3 \text{K}_2\text{O} \cdot 3 \text{H}_2\text{O}$	$\text{W}_6\text{As}_2\text{O}_{27}(\text{KO})_6(\text{HO})_6$
6 $\text{WO}_3 \cdot \text{As}_2\text{O}_5 \cdot 4(\text{NH}_4)_2\text{O} \cdot 2 \text{H}_2\text{O} + 3 \text{ aq}$	$\text{W}_6\text{As}_2\text{O}_{27}(\text{NH}_4\text{O})_8(\text{HO})_4 + 3 \text{ aq}$
16 $\text{WO}_3 \cdot \text{As}_2\text{O}_5 \cdot 6 \text{Ag}_2\text{O} + 11 \text{ aq}$	$\text{W}_{16}\text{As}_2\text{O}_{47}(\text{AgO})_{12} + 11 \text{ aq}$

In writing these formulas I have assumed that *all* the acids are 12-basic, since it has been shown that there are salts of the sixteen-, eighteen-, and twenty-atom series which correspond with this view. I shall resume the discussion of the subject in connection with the phospho-molybdates, and at the same time examine in detail the question of the existence of a distinct class of pyro-salts of the tungstic and molybdic series.

*(To be continued.)*

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## VII.

A THEORY OF THE CONSTITUTION OF THE SUN,  
FOUNDED UPON SPECTROSCOPIC OBSERVATIONS,  
ORIGINAL AND OTHER.

BY CHARLES S. HASTINGS.

Presented Oct. 13, 1880.

FRAUNHOFER discovered the lines in the solar spectrum, known by his name, in 1814. Many efforts to determine their origin followed. One of the most ingenious and carefully considered was that of Professor Forbes in 1836.\* He concluded that, if their origin is in the solar atmosphere, the light from the limb must exhibit stronger lines than that from the centre. His method was to examine the spectrum before and during an annular eclipse; as he found no recognizable change, his deduction was, "that the sun's atmosphere has nothing to do with the production of this singular phenomenon."

The point was again touched upon by Sir David Brewster and Dr. Gladstone in a joint study of the spectral lines, published in 1860.† Here "each of the authors came independently to the conclusion, that there is no perceptible difference in this respect between the light from the edge and that from the centre of the solar disk."

In 1867 Ångström ‡ repeated the experiment with negative results. Lockyer's § efforts also, in 1869, were attended with no better results.

In 1873, four years later, I devised and made an apparatus by which a perfect juxtaposition of the spectra of the centre and limb was secured. This apparatus and certain of the results gained by its use were described in a note "On a Comparison of the Spectra of the Limb and the Centre of the Sun," published in the American Journal of Science, (1873,) Vol. V. pp. 369-371. I was then a student at

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\* Note relative to the supposed Origin of the Deficient Rays in the Solar Spectrum. Phil. Trans., 1836, pp. 453-456.

† On the Lines of the Solar Spectrum. Phil. Trans., 1860, pp. 149-161.

‡ Phil. Mag., 1867, p. 76.

§ Proc. R. S., xvii. 350.



Yale College, and soon after left New Haven, when the research was necessarily interrupted. I hoped, however, that the novelty and interest of the observations might lead others, possessed of the necessary apparatus, to develop the results of this method of investigation. But as nothing has been published on this subject since that time, I was glad to have an opportunity to continue the investigation in the summers of 1879 and 1880. The results of my labor are embodied in this paper.

The method adopted in the recent observations is exactly the same as that described in the article cited; instead, however, of the equatorial of the Sheffield Scientific School, I used a Clark equatorial of 9.4 in. aperture and 120 in. focal length, which was kindly placed at my disposal by the gentlemen in Hartford to whom it belongs.\* The New Haven spectroscope, too, of twelve effective prisms, was replaced by one of which the dispersing member was a Rutherford grating on speculum metal, either of 8,648 or 17,296 lines to the inch, at will. These gratings were of the largest size, having a ruled surface of about  $1\frac{3}{4}$  in. square.

The immediate results I give in the order of the refrangibility of the lines observed, as no observed variations in them can be attributed to anything other than the temporary modifications of transparency in our atmosphere. The numbers are the places on Ångström's maps, as nearly as could be ascertained without a micrometer.

Line (C) 6561.8 is cleaner and wider at limb, i. e. the haze on either side of the line as ordinarily seen is much reduced.

6431 is slightly stronger at centre than at limb.

6371 is visible at centre, but not at limb.

(D<sub>1</sub>) 5894.8 slightly less hazy at limb.

(D<sub>2</sub>) 5889.0 decidedly cleaner at limb.

A fine line very close to its more refrangible side is either wanting or much fainter in spectrum of limb.

5577.5 is much stronger at limb.

5440  $\pm$  (not on Ångström's chart) is a little stronger at limb.

The Mg. lines 5183.0, 5172.0, 5166.5 ( $b_1$   $b_2$   $b_4$ ) are cleaner at limb. The line  $b_3$ , belonging to a different element, does not show such a peculiarity.

5045 (a faint line not in Ångström) is stronger at limb.

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\* My acknowledgments for this courtesy are gratefully accorded to Mr. Edgcomb, its former owner, and to Mr. Howard and Mr. Chapin, its present owners.

4919  $\pm$ , a faint line slightly stronger at limb.

(F) 4860.6 is much cleaner, more free from haze at limb.

4702.3 seems cleaner at limb.

4340.0 cleaner at limb.

4226.4 shows less haze at limb.

4101.2 is a very hazy line, so represented by Ångström, but at limb i is practically free from haze, — a striking difference.

4045 is slightly less hazy at limb.

Other differences have been recorded, but only these have been observed more than once each.

Any theory of the sun, worthy of attention, must not only explain the above-described phenomena, but also others better known, and as yet not accounted for satisfactorily. Of these the most noteworthy is the spectroscopic appearance of a spot and its penumbra. As is well known, such a spectrum exhibits a very strong general absorption, with a very slightly modified elective absorption. A few faint lines appear in the spot spectrum which are not otherwise seen; and a few faint lines of the ordinary spectrum are strengthened. A careful examination has persuaded me that the spectrum of a spot differs from that of the unbroken photosphere, just as the spectrum of the limb differs from that of the centre of the disk, save that the variations are more pronounced. Indeed, I could have considerably extended the list of lines strengthened at limb by an examination of the spot spectrum, where the variations appeal to the eye more clearly.

The accepted theory of the spots attributes the phenomenon to the absorption of the solar light by cooler, denser gases of the same nature as those producing the Fraunhofer lines. Familiar experiments teach, however, that, as the density of a gas increases, the change in the character of its radiation is shown in its spectrum by the broadening of its distinctive spectral lines, which at the same time grow more ill defined. Therefore it follows that, according to the law connecting radiation and absorption, dark lines produced by such a gas must also, under similar conditions, show increased breadth and diminished sharpness. That no such changes are to be recognized, is a fatal objection to the theory.

Another class of unexplained phenomena is the duplicity of certain lines of the solar spectrum, lines which are single in the spectra of terrestrial sources. Of these Professor Young has discovered  $E_1$ ,  $b_3$ , and  $b_4$ , with others.

My own observations can be arranged very simply in classes, and will then better lend themselves to theoretical discussion.

I. The most important fact of all is that the differences in the two spectra of centre and limb are extremely minute, escaping all but the most perfect instruments, and all methods which do not place them in close juxtaposition.

II. Certain lines, the thickest and darkest in the spectrum, notably those of hydrogen, magnesium, and sodium, which appear with haze on either side, in the spectrum of the centre of the solar disk, are deprived of this accompaniment in that of the limb.

III. Certain very fine lines (four observed) are stronger at limb.

IV. Other very fine lines (two or three observed) are stronger at centre.

The ordinarily accepted theory of the origin of the Fraunhofer lines fails to explain the phenomena as observed. That is, if we suppose the photosphere, whether solid, liquid, gaseous, or cloud-like, to yield a continuous spectrum which is modified only by the selective absorption of a surrounding atmosphere, then the absorption must be greater at the limb than at the centre of the solar disk; and this must be true independently of the thickness of that atmosphere, as well as of the form, rough or otherwise, of the surface of the photosphere. This evident consequence, pointed out in the first place by Forbes, nearly half a century ago, cannot be avoided. There is but one way of maintaining the theory and escaping Forbes's conclusion already quoted, and that the course pursued by Kirchhoff in the original statement of his theory of the solar constitution,\* namely, by assuming that the depth of the reversing atmosphere is not small compared to the radius of the sun. But innumerable observations during the score of years which have lapsed since that time prove that such a reversing atmosphere must be very thin. The famous observation of Professor Young during the total eclipse of 1870, when he saw appreciably all the Fraunhofer lines reversed, has naturally been received as the strongest confirmation of Kirchhoff's views as to the locus of the origin of the dark lines. But this very observation restricts the effective atmosphere (save for hydrogen and one or two other substances) to a depth of not more than 2". Thus, singularly enough, the very observation which led to the firmest belief among spectroscopists in the correctness of Kirchhoff's view exposed, at the same time, its most vulnerable point.

Another theory of the solar constitution, that of Faye, assigns a different seat to the stratum producing the Fraunhofer lines, namely,

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\* Untersuchungen über das Sonnenspectrum, (Berlin, 1862,) pp. 14, 15.

the photosphere itself. Regarding the principal radiation of the sun as coming from solid or liquid particles floating in a gaseous medium, the cloud-like stratum thus formed is necessarily somewhat transparent. According to his views, these particles are the sources of the continuous spectrum, and the medium in which they float is the locus of the selective absorption.\* Thus he attempts to reconcile the general theory of Kirchhoff with the observations and deductions of Forbes, which, as we have seen, were a constant stumbling-block in the way of accepting Kirchhoff's explanation.

Lockyer seems to have accepted this theory, and to have defended it in the earlier portion of his work; † but in 1872, after Young's important observation of 1870 and its confirmation in 1871, he changed his views, and regarded the layer just outside the photosphere as the true seat of the selective absorption producing the Fraunhofer lines. ‡ I supposed in 1873 that my observations then published could be explained on Faye's hypothesis.

There is, however, a fatal objection to the explanation as given by this theory. If the luminous particles are precipitated from the vapors of the photosphere, they cannot be at a higher temperature than the circumbient gases; on the contrary, on account of their greater radiating power, they must be slightly cooler. But the fundamental theory of absorption demands a lower temperature for the vapor producing dark lines than that of the principal source of light behind it; consequently this view of Faye cannot be accepted without great modifications.

Before advancing any theory of my own, it may be well to emphasize two principles taught by the theory of absorption, to which all hypotheses must be conformable. That Faye's fails in this is sufficient cause for its rejection.

1. To produce dark lines in a spectrum by absorption, the source of absorbed light *must* be at a higher temperature than that of the absorbing medium.

2. There is an inferior limit of brightness, below which the source of absorbed light cannot go without the spectral lines becoming bright.

Of these, the first is familiar, and requires here neither proof nor

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\* Comptes Rendus, lx., 1865.

† See "A Lecture delivered at the Royal Institution," May 28, 1869, quoted in Lockyer's *Solar Physics*, pp. 220, 221; also "The Rede Lecture," May 24, 1871, quoted in *Solar Physics*, pp. 317, 318.

‡ See revised report of two lectures delivered at Newcastle-upon-Tyne in October, 1872, *Solar Physics*, p. 409.

comment; the second, though not less evident, is less familiar because less important. As we shall make use of it, however, it may be well to enforce it by reference to common experience. Were it not true, it would be impossible to see bright lines in the spectrum of any flame to which daylight had access, for in this case the conditions demanded by the first principle are fully met, the sun being the origin of the daylight. That we do not see absorption lines is due then alone to the lack of necessary brilliancy in the daylight.

Thus much premised, we can frame a theory which explains all the observed phenomena exhibited by the spectroscope, and is also rendered highly probable by the revelations of the telescope.

As is well known, the solar surface, when examined with a powerful telescope of large aperture, presents a granulated appearance, the granules in general subtending an angle of a fraction of a second only. Probably this appearance is better known to the majority of astronomers by means of Professor Langley's admirable drawings,\* rather than by personal observation. These granules I regard as marking the locus of currents directed generally from the centre of the sun. About these currents are necessarily currents in an opposite direction, which serve to maintain a general equilibrium in the distribution of mass. Let us consider the action of such an ascending current. Starting from a low level at a temperature which we may regard as above the vaporizing point of all elements contained in it, as it rises to higher levels, it cools, partly by radiation, more by expansion, until finally the temperature falls to the boiling point of one or more of the substances present. Here such substances are precipitated in the form of a cloud of fine particles, which are carried on suspended in the current. The change of state marked by the precipitation is accompanied by a sudden increase in radiating power; hence these particles rapidly lose a portion of their heat, and become relatively dark, to remain so until they are returned to lower levels by the currents in a reverse direction.

In this theory, it will be observed, there is nothing which does violence to our accepted notions of the solar constitution. Indeed, it differs chiefly from that of Faye in localizing the phenomena of precipitation, instead of regarding it as proper to all portions of the photosphere; and, what is quite as important, in supposing the precipitation confined to one or two elements only. I shall attempt to define these elements farther on.

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\* *Am. Jour. Sci.*, Vol. VII, 1874, and Vol. IX, 1875, Plates.

In our theory, then, the granules are those portions of upward currents where precipitation is most active, while the darker portions, between these bodies, are where the cooler products of this change with accompanying vapors are sinking to lower levels.

Having stated the theory, we will now apply it to the four classes of phenomena defined above.

From the nature of the condensation the granules or cloudy masses must be very transparent, because the condensation is confined to elements which have very high boiling-points, and because such elements can be but a portion, perhaps but a small portion, of the whole matter contained in the upward currents. It is not *a priori* improbable that we receive light from many hundreds of miles below the general outer surface of the photosphere. Since these cloud-like sources of intenser radiations are surrounded on all sides by descending currents of colder vapors, *all* the white light which comes to us must have passed through media capable of modifying it by selective absorption. Again, since at the centre of the solar disk we can see as far into the photosphere as at the limb, and practically no farther, the phenomena of absorption ought to be, on the whole, the same in both regions.

Thus the fundamental and most important class of phenomena above classified finds a simple and logical explanation.

With regard to the phenomena of Class II. we have but to define the problem in order to find the solution at hand. All the lines of Class II. belong to vapors which lie high in the solar atmosphere, as is evident from their frequent reversal in the chromosphere. On the centre of the disk these lines are hazy or "winged," but not so at the limb. To the spectroscopist this aspect is characteristic of greater pressure, that is, of more frequent molecular impact. The observation then proves that the dark lines of hydrogen, magnesium, sodium, etc., as seen at the centre of the solar disk, are produced by the elements in question at a higher pressure than the corresponding lines at the limb. Accepting our theory, this must be so; for, supposing the transparency of the photosphere is such that we can see into it a distance of 2,000 miles, then at the centre of the disk we have light modified by selective absorption all the way from the extreme outer chromosphere down to 2,000 miles below the upper level of the photosphere; while 10" from the limb the light, though coming from the same depth of vapor measured along the line of vision, has its lowest origin more than 1,700 miles farther from the sun's centre than in the previous case. Of course the numbers here used have no definite significance,

but, modify them as we will, within the bounds of probability, the reasoning remains the same.

Suppose now a certain vapor which is confined to the upper stratum of the photosphere, or, rather, one of which the lower limit is thus restricted; then, according to the reasoning of Forbes, the force of which has been shown, its absorption lines ought to be strongest at the limb. This is the condition which produces the phenomena of Class III.

Before discussing the final class, we must recall a fact familiar to the most casual observer of the sun, namely, that lying upon the photosphere is a stratum producing a very strong general absorption, so strong indeed that the disk is probably less than a fourth as brilliant near the edge as at the centre. This layer is *very thin*, as proved by the great difference in brilliancy between the upper and lower portions of faculæ.

Since the difference of absorption at the two levels is very great, the conclusion follows, because the facula itself is so low that it rarely, if ever, appears as a projection on the limb of the sun. For convenience let us call this layer A.

Imagine then, a stratum of vapors, B, above the layer just described, which are not represented at all in the photosphere, and which are of nearly the same temperature as this layer A.\* Then (for the sake of simplicity regarding this layer as having no elective absorption) suppose all beneath the two spherical shells in consideration to be removed. In the spectroscope, light from such a source as the two layers A and B would yield a continuous spectrum; for the inner shell (A), radiating only white light, would be robbed of nothing not supplied in equal quantity by radiation from the outer shell (B), since they are of the same temperature. If such layers as these really do exist about the sun, we can now readily state the appearances which would be presented by a sun so constituted, if the three-fold system should be studied spectroscopically. In the centre of the projected disk, the lines proper to the exterior shell (B) would be

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\* This supposition is not opposed to probability, for though we must regard the temperature as generally decreasing in passing from the photosphere outward, it does not follow that this decrease is continuous. A similar general law may be stated for our own atmosphere, but in a clear night the air in the immediate vicinity of the ground is colder than that just above. The explanation of this phenomenon is familiar in the theory of dew and hoar-frost. Analogous causes for irregularity in the distribution of temperature in the solar atmosphere must be even more efficacious, since the layer A is probably a more vigorous radiator than the earth, and the gases above it are certainly far more diathermous than our atmosphere.



reversed, i. e. dark. As we approached the edge, however, *owing to the opacity of the inner shell*, the conditions would approximate to what they would be if the layers A and B existed alone, the central body being removed, and the lines would fade; if faint, they would vanish. This is our explanation of the phenomena of Class IV.

Every theory involves certain conditions. We finally judge of the soundness or unsoundness of any theory largely from the consideration of these implied conditions, and of the extent to which they are fulfilled by it. For instance, our explanation of the fact that certain very fine lines are stronger at the centre (IV.) demands that the substances giving such lines should be found in the chromosphere, indeed mainly restricted to the chromosphere. Fortunately I can say that one of them (6371), which I first discovered and measured carefully, is identical with the fourteenth line of Young's second Catalogue of Chromosphere Lines. The other one, the wave-length of which I took from Ångström's chart without correction, may correspond with Young's ninth (6429.9) line of the same Catalogue, which differs in place by only one sixth the distance between the *D* lines. This I shall test at the earliest opportunity.

If the theory I have proposed is correct, it affords the first definite evidence of the existence of *chemical compounds* in the sun, for in accordance with it the lines of Class III. and Class IV. belong to substances which are not found in the lower photosphere. We know however that all gases must increase in density in passing from their outer limit towards the centre of the sun; and we have seen a proof of this in the case of hydrogen and certain other vapors in the discussion of our observations, which showed that the characteristic lines indicated greater density when they originated at greater depths. The only escape from the contradiction is in the assumption that the lines of the last two cases (III., IV.) are due to compound vapors having a dissociation temperature below that of the lower photosphere. Of course, the substances of Class IV. have a lower dissociation temperature than those of Class III.

A naturally suggested and legitimate subject of speculation is as to the nature of the substance which, by precipitation, forms the cloud-masses of the photosphere. We may predicate three properties with greater or less positiveness, viz.:—

1st. The substance has a boiling-point above that of iron, for iron vapor at a lower temperature exists in the immediate neighborhood.

2d. The molecular weight is probably not great; for, though precipitated below the upper natural limit of its vapor, there are few ele-



ments found in abundance above it, and those in general of low vapor density.

3d. The element is not a rare one. Of these guides the last is perhaps of the least value.

The substances which apparently meet all these conditions are carbon and silicon: nor is it easy to name any other which will. Accepting for a moment as an hypothesis that the light coming from the sun is radiated by solid or liquid particles of carbon just at the point of vaporization, let us see if the facts of observation fulfil the implied conditions.

As a first consequence, we see that the temperature and light of the photosphere are defined as those of solid carbon at the point of volatilization. In the electric arc there is a very small area of the positive carbon pole at this high temperature. Though this area is in a very disadvantageous position for observation, and can consequently have but a disproportionately small share in producing the total effect, the splendor of the electric light might almost tempt us to believe the guess a valid one. Another consequence implied, however,—namely, that the spectral lines proper to simple carbon are absent in the solar spectrum,—is doubtless better adapted as a crucial test of the hypothesis than a study of the electric light. There has been evidence recently offered that carbon lines are present in the solar spectrum. Granting this, we perceive that the photosphere contains solid or liquid particles hotter than carbon vapor, and consequently not carbon.

I am then inclined to suspect that the photospheric material may be silicon, which, though denser in the gaseous state than carbon, is not improbably more abundant. There is also good reason to suppose that carbon is precipitated at a higher level; and the analogous but less common element boron may add a minor effect.

In the explanations which I shall give of the remaining phenomena, it may serve to fix the ideas, to think of the granules which characterize the sun's photosphere as clouds of a substance like precipitated silicon. At any rate, we are sure that the substance in question, so far as we know it, has properties similar to those of the carbon group.

I have given plausible explanations of all the phenomena included specially in my own observations. It remains to discuss the others, briefly mentioned above.

The substance precipitated cools very rapidly, as it is an excellent radiator separated from space only by extremely diathermous media. It forms then a smoke-like envelope, which ought to exert just such a general absorption as that observed at the limb of the sun. It is thin

because of the relatively great density of the substance in the liquid or solid state; thus the apparent brilliancy of the faculæ is readily understood.

If there is any disturbing cause which would tend to direct currents of gas, over a considerable area of the solar surface, toward a point, this smoke, instead of quietly settling down to lower levels between the granules, would concentrate about this point, there exercising a marked general absorption which would betray itself as a spot. At this place the suspended particles would sink to lower levels with constantly increasing temperature, until finally, heated to intense incandescence, they would revolatilize. Thus the floor or substratum of every spot must be a portion, depressed it is true, of the photosphere. All the spectroscopic phenomena of spots, which have proved so perplexing, are thus naturally and easily explained.

\* In the immediate neighborhood of a spot, the centripetal currents bend down the ordinary convection or granule-producing currents, so that they are approximately level. Before, the latter cooled suddenly by rarefaction in their upward course; now, they cool mainly by the much slower process of radiation; thus, while before the locus of precipitation was restricted, it is now greatly extended. This is the cause of the great elongation of the granules in the penumbra, — a real elongation, I imagine, and not merely an apparent one.

Finally, concerning the close duplicity of certain lines, we may reason thus: — If we could surround the sun by a stratum of gas hotter than the photosphere and much rarer than that producing the corresponding Fraunhofer lines, we should, as is shown by a course of reasoning which I have given in another place,\* see each dark line divided by a sharp bright line in its centre, that is, doubled. But as a consequence of the theory this supposed condition must be practically met in the case of certain vapors in the sun. The gases just over the granules, in the vertical currents, are at a very high temperature, essentially that of the condensing material itself, consequently much hotter and rarer than the relatively low-lying vapors which, as we have seen, produce the Fraunhofer lines.

There are, however, certain evident limitations to these conditions; in other words, we cannot expect to see all the dark lines doubled by any increase of dispersive power. For instance, a line must have a marked tendency to broaden with increased pressure, otherwise the duplication cannot be pronounced. Again, the layer of rare vapor must

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\* On Lockyer's Hypothesis. *Am. Jour. Chem.*, i. 15.

be thin, or its temperature cannot be relatively high throughout, as demanded by the theory. This evident condition doubtless gives the reason why the hydrogen lines, though the broadest in the solar spectrum, are not sensibly double.

The theory of the constitution of the sun above proposed may be briefly recapitulated thus:—

Convection currents, directed generally from the centre of the sun, start from a lower level, where the temperature is probably above the vaporizing temperature of every substance. As these currents move upward they are cooled, mainly by expansion, until a certain element (probably of the carbon group) is precipitated. This precipitation, restricted from the nature of the action, forms the well-known granules. There is nothing which has come under my observation which would indicate a columnar form in these granules under ordinary circumstances.

The precipitated material rapidly cools, on account of its great radiating power, and forms a fog or smoke, which settles slowly through the spaces between the granules till revolatilized below. It is this smoke which produces the general absorption at the limb, and the "rice-grain" structure of the photosphere.

When any disturbance tends to increase a downward convection current, there is a rush of vapors at the outer surface of the photosphere toward this point. These horizontal currents, or winds, carry with them the cooled products of precipitation, which, accumulating above, dissolves slowly below in sinking. This body of smoke forms the solar spot.

The upward convection currents in the region of the spots are bent horizontally by the centripetal winds. Yielding their heat now by the relatively slow process of radiation, the loci of precipitation are much elongated, thus giving the region immediately surrounding a spot the characteristic radial structure of the penumbra.

This conception of the nature of the penumbra implies a ready interpretation of a remarkable phenomenon, amply attested by the most skilful observers, and, as far as my knowledge goes, wholly unexplained; namely, the brightening of the inner edge of the penumbra in every well-developed spot.\*

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\* Relating to this phenomenon we see important observations by Professor Langley, *Am. Jour. Sci.*, Vol. IX. (1875,) p. 194; also *Le Soleil*, par Le P. A. Secchi, Paris, 1875, Chap. IV. p. 81, and particularly Fig. 46, p. 90, with explanatory text.

This interpretation is perhaps most readily imparted by a comparison of the hot convection currents in the two cases. When the convection current is rising vertically, the medium is cooled by expansion until the precipitation temperature is reached, when all the condensible material appears *suddenly*, save as it is somewhat retarded by the heat liberated in the act. Immediately afterward the particles become relatively dark by radiation. In the horizontal currents a very different condition of things obtains. Here the medium does not cool dynamically by expansion, but only by radiation; hence, since the radiation of the solid particles is enormously greater than that of the supporting gas, practically by that of the particles themselves. Thus after the first particle appears, it must remain at its brightest incandescence until all the material of which it is composed is precipitated. From this we see that such a horizontal current must increase gradually in brilliancy to its maximum, and then suddenly diminish, — an exact accordance with the facts as observed.

JOHN HOPKINS UNIVERSITY, BALTIMORE,  
September, 1880.

## VIII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XIII.—ACOUSTIC PHENOMENON NOTICED IN A  
CROOKES' TUBE.

BY PROFESSOR CHAS. R. CROSS.

Presented Nov. 10, 1880.

A SHORT time since, while experimenting with a Crookes' tube, I noticed a phenomenon which was quite striking, and so evident that it hardly seems possible that it has not been observed before, though I have never seen any notice of the fact.

In working with the tube, in which a piece of sheet platinum is rendered incandescent by the concentration upon it of electrified particles repelled from a concave mirror, I noticed that when the mirror was made the negative electrode, so that this concentration took place, a clear and quite musical note issued from the tube. I thought at first that the pitch of this note would coincide with that produced by the circuit-breaker of the coil, which made about 120 breaks per second, but this did not prove to be the case, for very great changes in the rate of the circuit-breaker did not affect the note given by the tube. The effect seemed to be produced by the vibration of the sheet platinum under the influence of the molecular impact, which vibrations were communicated to the glass walls of the tube by the enamelled rod to which the platinum was attached. This gave rise to a sound somewhat resembling that caused by the pattering of rain against a window-pane, but higher in pitch and more musical. The sound changed its character very greatly when the direction of the current was reversed, only a feeble murmur being heard. I obtained a similar musical note, though far less loud, with the "mean free-path" tube, best when the middle plate was positive. With a tube containing phosphorescent sulphide of calcium the note was very dull

in its quality, and low in pitch, but still quite perceptible. With this tube a change in the direction of the current did not affect the note produced. I did not obtain this musical note from any tube that I possess in which the current enters and leaves by a straight wire, except in the case of one Geissler's tube exhausted so as to give stratifications, in which it was very feebly heard.

## IX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY  
OF HARVARD COLLEGE.

BY HENRY B. HILL.

Presented June 9, 1880.

FURFUROL, ONE OF THE PRODUCTS OF THE DRY DISTILLA-	
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In December, 1876, by the kind invitation of Dr. E. R. Squibb, I had the opportunity to examine the working of a new process for the manufacture of acetic acid by the dry distillation of wood at a low and carefully regulated temperature, as it was carried on under his direction at Brooklyn, N. Y. I then noticed that, in the rectification of the crude wood spirit, a yellowish oil passed over with the vapor of water after the more volatile portions had been distilled off. Its high specific gravity and its peculiar odor made me anxious to examine it more closely.

A short study of it was sufficient to show that it contained large quantities of furfural which could be isolated in a pure state with little trouble, and I therefore undertook at once the study of the constitution of furfural and pyromucic acid. Before my investigations were far advanced, Baeyer\* published the first of his papers upon the constitution of furfural, in consequence of which my own work was naturally discontinued. At the same time, however, I wrote to Professor Baeyer asking if I could not make use of the large supply of material which I had at hand without interfering with the plan of his research. In reply I received the extremely considerate intimation that a study of mucobromic acid and its derivatives would in no way interfere with his work.

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\* Berichte der deutsch. chem. Gesellsch., x. 355.

This investigation was begun in 1877; and, although it is not yet completed, so many facts have accumulated that I have thought it best to lay before the Academy the results already obtained.

Different portions of this research I have carried on with Mr. O. R. Jackson and Mr. C. F. Mabery, assistants in this laboratory, and with Mr. W. Z. Bennett. In my description of our results, I shall make plain the share which each of these gentlemen has had in the work.

My most sincere thanks are due to Dr. Squibb for the generous supply of material, without which it would have been impossible for me to have undertaken this investigation.

#### FURFUROL ONE OF THE PRODUCTS OF THE DRY DISTILLATION OF WOOD.

Although the products formed in the dry distillation of wood have repeatedly been made the subject of investigation, I can find in the literature of the subject but little reference to the presence of furfural among them. That furfural is thus formed is asserted by Gmelin\* on the authority of Völkel, but a close examination of Völkel's original papers† fails to show any sufficient foundation for the assertion. Although Völkel had already shown that furfural was formed in the dry distillation of sugar, and had established its presence by analysis,‡ in his subsequent work upon the dry distillation of wood he seems to have based his conclusions solely upon qualitative tests by no means conclusive. Although he makes a number of general statements concerning the presence of furfural among the products he obtained, I can find nothing more definite than is contained in the following passage.§

After describing the extraction of a yellowish brown oil from the pyroligneous acid by means of ether he proceeds: "In Kalilauge löst sich das Oel unter Entwicklung eines betäubenden Geruchs auf, der von einer geringen Menge einer organischen Basis herrührt, weil er auf Zusatz von Säure wieder verschwindet. Die dunkel gefärbte alkalische Lösung trübt sich in kurzer Zeit durch Ausscheiden eines gelbbraunen Körpers, der Pyroxanthin enthält. Aus der abfiltrirten noch stark gefärbten alkalischen Flüssigkeit wird durch verdünnte Schwefelsäure ein anderer brauner Körper abgeschieden, und zugleich

\* Gmelin's Handbuch, vii. 599; Suppl., ii. 972.

† Poggendorff's Annalen, lxxxi. 496; lxxxiii. 272 and 557; Ann. Chem. u. Pharm., lxxxvi. 66.

‡ Ann. Chem. u. Pharm., lxxxv. 59.

§ Ibid., lxxxvi. 83.



der Geruch des Kreosots wahrgenommen. Aus diesen Reactionen ergibt sich dass das Oel . . . ein sehr gemengtes . . . ist. Es enthält ein eigenthümliches Oel (Pyroxanthogen), das durch die Einwirkung von Alkalien in Pyroxanthin übergeht; Kreosot; ferner mehrere flüchtige Oele, die durch Alkalien in braune Körper umgeändert werden die in Kali theils löslich theils unlöslich sind. Diese letzteren Oele sind unstreitig identisch mit den flüchtigeren Oelen die bei der Destillation des Zuckers erhalten werden, Furfurol, u. s. w." I have quoted the passage with but little abbreviation, that the character of the qualitative tests upon which Völkel based his conclusion may be appreciated.

Quite recently since the publication of a preliminary note by me upon this subject, V. Meyer\* has found in the commercial glacial acetic acid of the continent, a small quantity of furfurol which manifested itself by the intense red color developed when the acid was mixed with aniline.

Although these two observations are all I can find recorded of the presence of furfurol among the products of the dry distillation of wood, its formation from wood by other means has been more frequently noticed. Although Döberciner† could obtain no furfurol from sawdust by distillation with sulphuric acid, Fownes‡ none from linen, and Cahours§ and Gudkow¶ were equally unsuccessful with pure cellulose, Emmet\*\* obtained it by the same method from woody fibre, Stenhouse†† from sawdust, afterward from mahogany‡‡ and madder.§§ Gr. Williams¶¶ also found that it was formed when wood was heated under pressure with water, although none could be obtained at ordinary pressures. Similar results were obtained by H. Müller.\*\*\*

A brief description of the method of distillation which has furnished the material for this investigation may prove of interest: since the product obtained in this way contains considerable quantities of furfurol, while the percentage formed by the ordinary methods must be

\* Berichte der deutsch. chem. Gesellsch., xi. 1870.

† Journ. pract. Chem., xlv. 168.

‡ Pharmaceutical Journal and Transactions, viii. 113.

§ Ann. Chim. Phys., [3] xxiv. 277.

¶ Zeitschr. für Chem., 1870, 360.

\*\* Ann. Jour., xxxii. 140.

†† Ann. Chem. u. Pharm., xxxv. 301.

‡‡ Ibid., lxxiv. 278.

§§ Ibid., lxxx. 325.

¶¶ Chem. News, xxvi. 231 and 293.

\*\*\* Ibid., xxvi. 247.

very small to have escaped notice so generally. The wood, chiefly oak, is cut into small pieces and filled into rectangular retorts of boiler iron, each one capable of holding a charge of from five to six thousand kilogrammes. The retorts when charged are placed in separate cells of an oven heated by hot-air flues. The temperature of this oven is carefully regulated by means of long mercurial thermometers built into each cell, and the thermometer readings vary from  $150^{\circ}$  at the beginning of a distillation to  $200^{\circ}$  at the end. The average time required is six days, and during this time the wood loses about thirty-two per cent of its weight. The volatile products pass through an outlet pipe at the top of each retort, and are condensed in a set of ordinary coolers.

The wood left in the retorts after distillation is darker in color and somewhat more brittle than the fresh wood: its composition agrees essentially with that given by Payen\* for dried oak wood. The specimens of wood for analysis were taken while still warm from the retorts, and kept hermetically sealed until analyzed.

- I. 0.4480 grm. substance gave 0.8950 grm.  $\text{CO}_2$ , 0.2545 grm.  $\text{H}_2\text{O}$  and 0.0040 grm. ash.
- II. 0.3880 grm. substance gave 0.7810 grm.  $\text{CO}_2$  and 0.2220 grm.  $\text{H}_2\text{O}$ . 1.2725 grm. of the same wood gave 0.0070 grm. ash.
- III. 0.3270 grm. substance gave 0.6390 grm.  $\text{CO}_2$ , 0.1740 grm.  $\text{H}_2\text{O}$  and 0.0015 grm. ash.

	I.	Found. II.	III.	Payen.
C.	50.01	54.89	53.30	54.44
H.	5.88	6.29	5.78	6.24
Ash.	0.89	0.55	0.46	

The volatile products of the distillation are subjected to the ordinary processes of rectification. In fractioning the wood spirit, after the more volatile portions have passed over, the distillate throws down a heavy yellow oil upon dilution with water, and somewhat later the slightly acid aqueous distillate contains an abundance of the same heavy oil in suspension. The quantity of oil which thus separates in the course of distillation amounts to between three and four tenths of one per cent of the crude wood spirit taken, although I am unable to form even an approximate estimate of what proportion this may be of the total amount present.

The oil, as I received it, was feebly acid to test paper, and had a

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\* N. Ann. Sci. Nat., xi. 24.

peculiar aromatic odor. It was bright yellow in color, and slightly heavier than water. It was washed with water dried over calcic chloride and submitted to fractional distillation. The liquid began to boil a little above  $100^{\circ}$ ; but the thermometer rose rapidly, and had reached  $160^{\circ}$  before any considerable quantity had passed over; between  $160^{\circ}$ – $170^{\circ}$  it remained stationary for a long time, and then rose again rapidly to over  $200^{\circ}$ . After several distillations, about sixty per cent of the oil taken distilled between  $160^{\circ}$  and  $165^{\circ}$ , the greater part of which boiled steadily at  $162^{\circ}$ . The boiling point and general character of the oil at once suggested the presence of furfural, and this was readily proved by its conversion into furfuramide, furfurine, and pyromucic acid. The behavior of the oil to alkalis, however, showed that it was still by no means homogeneous. When shaken with a dilute solution of potassic or sodic hydrate, a brilliant yellow color was developed; and in a few moments the clear liquid became turbid with the separation of a flocculent yellow precipitate, which proved to be chiefly pyroxanthin. In following out the method of purification which was thus suggested, I found it most convenient to separate from the crude oil, only so much of the higher boiling constituents as could be removed by rejecting that which passed over above  $175^{\circ}$  in two successive distillations. The distillate collected below  $175^{\circ}$  was then gradually mixed with one-fourth its volume of a concentrated solution of sodic hydrate, taking care to keep the mixture cool, and shaking the two well together. After standing a short time, the oil was separated from the alkaline solution, washed with a little water, and distilled with steam. The furfural thus obtained was sufficiently pure for all ordinary purposes, and from such a product was made all the pyromucic acid which has been used in the course of the following investigations.

For its conversion into pyromucic acid, it was mixed with an equal volume of a concentrated alcoholic solution of sodic hydrate, and carefully stirred until the violent reaction was over. The sodium salt was then thoroughly washed with ether, dissolved in hot water, and decomposed by concentrated hydrochloric acid. For the purification of the crude acid, it was dissolved in a cold dilute solution of sodic carbonate, taking care that the solution should remain slightly acid. The filtered solution of the sodium salt was boiled with bone-black filtered, concentrated by evaporation, and finally acidified with hydrochloric acid. The acid which separated on cooling was then recrystallized from boiling water, and was found on analysis to be sufficiently pure for further use.

0.8140 grm. substance gave 1.5910 grm.  $\text{CO}_2$  and 0.2910 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_8\text{H}_4\text{O}_8$	Found.
C	53.57	53.31
H	3.57	3.97

The acid prepared in this way melted at  $128-129^\circ$ ; and, since the melting point of pyromucic acid is usually given somewhat higher, it seemed advisable to subject this product to further purification. Mr. J. J. Thomsen, therefore, prepared the ethyl-ether of the acid by saturating its solution in absolute alcohol with hydrochloric acid, precipitating with water, and washing first with a dilute solution of sodic carbonate and then with water. He then found that the carefully dried ether distilled from the first drop to the last unchanged at  $195^\circ$  (Mercury column completely in vapor) under a pressure of 766 mm. On cooling, it crystallized in large transparent prisms, which melted at  $34^\circ$ . According to Malaguti,\* ethyl pyromucate melts at  $34^\circ$ , but boils at  $208-210^\circ$ , under a pressure of 756 mm. For the determination of boiling point, we employed about 30 grm. of the ether, and an analysis showed its purity.

0.5615 grm. of substance gave 1.2330 grm.  $\text{CO}_2$  and 0.2940 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{12}\text{H}_8\text{O}_{12}\text{C}_2\text{H}_5$	Found.
C	60.00	59.8
H	5.71	5.81

A portion of this ether was saponified with sodic hydrate, the acid liberated from the sodic salt, recrystallized from hot water several times, and finally melted. The solidified acid melted at  $130^\circ.5$  (uncom.), while an acid made directly from mucic acid melted at  $130^\circ$ . The corrected melting points of the two were  $133^\circ$  and  $132^\circ.5$ ; whereas Schwanert† gives the corrected melting points  $134^\circ.3$  and  $132^\circ.6$  respectively for substance made from furfural and from mucic acid. The chief constituent of the oil under investigation was thus shown to be furfural. From the higher boiling portions, I have as yet been able to isolate no well-marked substances. On distillation, the thermometer rose slowly to over  $300^\circ$ , and even after long fractioning there appeared to be no tendency towards constant boiling points. By far the greater portion was insoluble in alkalies, and I could obtain no characteristic derivatives by the action of various reagents.

\* Ann. Chim. Phys., [2] lxiv. 279.

† Ann. Chem. u. Pharm., cxvi. 257.

From the sodic hydrate used for washing the crude furfural could be separated in small quantity an oil volatile with steam, and possessing a strong odor like smoked fish. It had the general characters of a phenol, but I have not as yet further identified it. Since a large quantity of material has been accumulated in preparing the furfural necessary for the following researches, I hope before long to make further study of the less volatile constituents which are present in smaller quantity.

#### PYROXANTHIN.

I have already mentioned the yellow flocculent precipitate, formed by the action of alkalies upon the crude furfural, which upon examination proved to consist chiefly of pyroxanthin. This substance was discovered in 1835 by Dr. Scanlan,\* of Dublin, in the residue from the preparation of methyl alcohol from crude wood spirit by means of lime. In 1836, it was further studied by Apjohn and Gregory, † who deduced from their analyses the formula  $C_{21}H_{18}O_4$ , although they did not succeed in confirming this formula by the preparation and analysis of any of its derivatives. This formula was subsequently changed to  $C_{10}H_8O_2$  by Gmelin, ‡ although this change was apparently not based upon any further experimental work. Although I have not as yet had any very considerable quantity of material at my command, I have studied some of its reactions and prepared two well-marked bromine derivatives whose percentage composition necessitates the adoption of the formula  $C_{15}H_{12}O_3$ .

In the method I have described for the purification of the crude furfural, after that portion which is volatile with steam has been distilled off, there remains a red viscous oil in the retort, which, on cooling, partially solidifies. If this semi-solid mass is then treated with small quantities of cold alcohol, the red oil, which results, in part at least, from the action of the sodic hydrate upon the furfural, dissolves, while the greater part of the pyroxanthin is left behind in minute crystals. Occasionally, this viscous residue crystallizes only after the addition of the alcohol and vigorous stirring. The pyroxanthin seems to be more neatly separated, if the furfural is slightly acidified with acetic acid after separating the alkaline solution before distilling with steam. After the crystals have been well washed with

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\* Phil. Mag., [3] xli. 395.

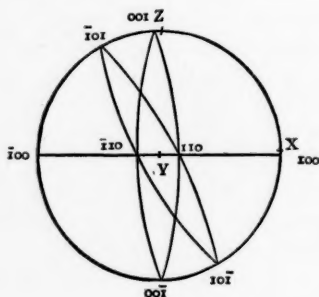
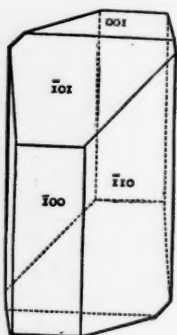
† Royal Irish Acad. Proc., 1836, xxxiii. Ann. Chem. u. Pharm., xxi. 143.

‡ Gmelin's Handbuch, vii. 167.

cold alcohol, they are recrystallized from boiling alcohol until the substance has a bright, clear, orange-yellow color. Boiling the alcoholic solution with bone-black facilitates the removal of the red impurities.

Pyroxanthin is completely insoluble in water, and very sparingly soluble in ether or carbonic disulphide; in hot alcohol, benzol, or glacial acetic acid it dissolves abundantly, and crystallizes in well-developed forms on cooling. From alcohol it crystallizes in small, brilliant, orange-yellow needles with a blue reflex; from benzol in tolerably large reddish-yellow monoclinic prisms; and from glacial acetic acids in flat radiated needles, which are formed by the development of the prism in the direction of the orthodiagonal. The crystallographic examination which I made of the substance gave the following results.

#### CRYSTALLINE FORM OF PYROXANTHIN.



#### *Monoclinic System.*

Forms observed {001} {101} {100} {110}.

$$a : b : c = 2.748 : 1 : 1.413 \quad ac = 87^\circ 56'$$

#### *Angles between Normals.*

	Found.	Calculated.
110 : 110	40° 1'	Fundamental angles.
101 : 001	26° 46'	
101 : 100	61° 10'	
110 : 100	69° 54'	69° 59'
110 : 101	80° 25'	80° 30'

For analysis the substance was crystallized from alcohol and dried at 100°.

- I. 0.2673 grm. substance gave 0.7341 grm. CO<sub>2</sub> and 0.1279 grm. H<sub>2</sub>O.  
 II. 0.2432 grm. substance gave 0.6690 grm. CO<sub>2</sub> and 0.1141 grm. H<sub>2</sub>O.

Calculated for C <sub>15</sub> H <sub>13</sub> O <sub>3</sub> .		Found.		Apjohn and Gregory.
		I.	II.	
C	75.00	74.91	75.01	74.27
H	5.00	5.31	5.25	5.61

Since the substance was very refractory and needed a high temperature in a stream of oxygen for complete combustion, my results show a sufficiently close agreement with those of Apjohn and Gregory.

This substance melts at 162° and volatilizes with partial decomposition at a higher temperature, although it may be sublimed without difficulty by careful heating in a current of air. In concentrated sulphuric acid it dissolves with an intense purple, and in hydrochloric or hydrobromic acid with a crimson color. From these solutions water precipitates the substance apparently unchanged. In alkaline solutions it is completely insoluble, and by melting caustic potash it is merely carbonized. Bromine attacks it vigorously, and, under certain conditions, forms well-crystallized products.

*Dibrompyroxanthintetabromide*, C<sub>8</sub>H<sub>10</sub>Br<sub>2</sub>O<sub>3</sub>Br<sub>4</sub>. When pyroxanthin is suspended in ten times its weight of carbonic disulphide, and three and a half parts of bromide diluted with an equal weight of carbonic disulphide are added, the pyroxanthin instantly dissolves and forms a clear deep-red solution. After standing for a short time, clouds of hydrobromic acid are given off, and soon after the separation of a beautifully crystalline substance begins. After twenty-four hours the carbonic disulphide is poured off, and the crystals which have separated are thoroughly washed with ether. For analysis I recrystallized the substance from boiling chloroform and dried it *in vacuo*.

- I. 0.5598 grm. substance gave 0.5136 grm. CO<sub>2</sub> and 0.0842 grm. H<sub>2</sub>O.  
 II. 0.6814 grm. substance gave 0.5758 grm. CO<sub>2</sub> and 0.0845 grm. H<sub>2</sub>O.  
 III. 0.3094 grm. substance gave 0.4884 grm. AgBr.\*  
 IV. 0.3128 grm. substance gave 0.4936 grm. AgBr.

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\* All the determinations of halogens in this and the subsequent investigations were made according to the method of Carius. In most cases the asbestos

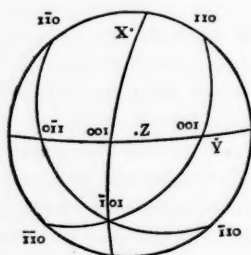
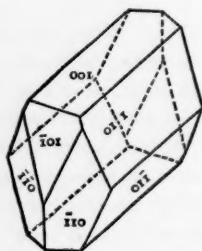


Calculated for $C_{13}H_{10}Br_6O_8$ .		Found.			
		I.	II.	III.	IV.
C	25.07	25.02	24.87		
H	1.39	1.67	1.49		
Br	66.85			67.16	67.18

These percentages agree closely with those required by the formula  $C_{13}H_{10}Br_6O_8$ , and the behavior of the substance is such that it must be considered dibrompyroxanthintetrabromide. It crystallizes in small, brilliant, colorless prisms which belong to the triclinic system. On heating, it is decomposed below  $100^\circ$  with carbonization and the evolution of hydrobromic acid. It is very sparingly soluble in ether or carbonic disulphide; in boiling benzol or chloroform it dissolves quite freely, and the greater part again separates on cooling. In cold alcohol or glacial acetic acid, it is sparingly soluble; but, on warming, it dissolves with decomposition and then forms a yellow solution. In the cold, it is unaltered by concentrated sulphuric acid; on heating, it is carbonized.

A crystallographic study of the substance gave the following results:—

#### CRYSTALLINE FORM OF DIBROMPYROXANTHINTETRABROMIDE.



#### *Triclinic System.*

Forms observed,  $\{001\}$   $\{011\}$   $\{01\bar{1}\}$   $\{110\}$   $\{\bar{1}10\}$   $\{101\}$ .

$$a : b : c = 0.733 : 1 : 2.370.$$

$$bc = 74^\circ 43'; ac = 83^\circ 40'; ab = 96^\circ 46'.$$

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filter of Dr. Gooch was used. The great saving of time and labor as well as the increased accuracy attainable by this method renders it invaluable in determinations of this sort.



*Angles between Normals.*

Found.		Calculated.
OI1 : II0 . . . .	47° 15'	Fundamental angles.
OI1 : IO1	69° 50'	
OI1 : O11	135° 27'	
II0 : IO1	34° 18'	
II0 : I10	76° 57'	
IO1 : I10	48° 49'	48° 58'
I10 : O1I	61° 14'	61° 12'
I10 : O11	58° 6'	57° 41'
O01 : II0	73° 59'	74° 18'
O01 : I10	93° 8'	93° 41'
O01 : OI1	54° 6'	53° 49'
O01 : O11	81° 21'	81° 38'
O01 : IO1	63° 37'	63° 57'

Bromine when moderately diluted with carbonic disulphide has no further action upon this substance. It is attacked, however, when exposed to the vapors of bromine, and deliquesces rapidly, forming a dark-red syrup, which over lime *in vacuo* gradually solidifies. From this product I have as yet been unable to isolate any substance with characters sufficiently well marked to encourage further study.

*Dibrompyroxanthin*,  $C_{15}H_{10}Br_2O_8$ . The subtraction of bromine, on the other hand, gave a beautifully crystalline product with sharply marked characteristics. This substance I first made by the action of phenol. If the dibrompyroxanthintetrabromide is gently warmed with a little phenol, to which sufficient water has been added to keep it liquid, it dissolves, forming a highly colored solution, which is red by transmitted and green by reflected light. If alcohol is then added, it causes the separation of an abundance of fine, felted brilliant-yellow needles, which may be recrystallized from alcohol. This same substance may also be made by boiling the tetrabromide with absolute alcohol, and adding zinc dust or finely powdered metallic antimony. The latter method is perhaps most advantageous, since little or no product is obtained if the phenol solution is too strongly heated, or, if the zinc dust contains a large percentage of oxide. For analysis, the substance was dried at 100° after several recrystallizations from alcohol. The material used in analyses I. and II. was made with phenol, while that used in analysis III. was made with antimony.

- I. 0.3816 grm. substance gave 0.6333 grm.  $\text{CO}_2$  and 0.0918 grm.  $\text{H}_2\text{O}$ .  
 II. 0.3137 grm. substance gave 0.2978 grm. AgBr.  
 III. 0.2577 grm. substance gave 0.2419 grm. AgBr.

Calculated for  $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{O}_3$ .

		I.	Found. II.	III.
C	44.22	45.25		
H	2.51	2.67		
Br	40.20		40.40	39.94

The analyses showed that the substance was dibrompyroxanthin, and that it was formed from the bromine derivative already described by the subtraction of bromine.

In hot alcohol it dissolves readily, although in cold it is sparingly soluble. It is quite soluble in ether or carbonic disulphide, and very readily in benzol, chloroform, or glacial acetic acid.

From a solution in warm chloroform, it crystallizes in large, compact, twinned forms of the monoclinic system, which are dichroic. In concentrated sulphuric acid, it dissolves with an intense, pure blue color. This blue solution, on dilution with water, throws down a yellow precipitate, which is apparently the unchanged substance. If quickly heated upon platinum foil, it melts to a perfectly clear yellow liquid; but it is impossible to determine its melting point, since it decomposes and carbonizes when its temperature is more gradually raised. A solution in carbonic disulphide, when mixed with bromine, gradually deposits well-formed crystals of the tetrabromide. This simple substitution product I have not succeeded in making directly from pyroxanthin. In every case where a smaller quantity of bromine was employed, the addition product was still formed, and a part of the pyroxanthin remained unaltered.

I have also studied the action of aqueous bromine, but have not been successful in obtaining any definite products. If pyroxanthin is suspended in water, and bromine gradually added, or the vapors of bromine carried in by a current of air, a white amorphous substance is slowly formed, which is almost insoluble in water, but extremely soluble in other ordinary solvents. By evaporation of such solutions, the substance again separates in an amorphous condition. In alkalies it dissolves, forming a deep-brown solution, from which nothing can be precipitated by the addition of acids.

Since there appeared to be little hope of effecting its purification by ordinary methods, I proceeded to analyze carefully prepared material.

I found, however, that the substance turned brown on standing over sulphuric acid, and the analysis of two different preparations showed conclusively that no constant results could be obtained in this way.

- I. 0.3726 grm. substance gave 0.3142 grm.  $\text{CO}_2$  and 0.0594 grm.  $\text{H}_2\text{O}$ .
- II. 0.2016 grm. of the same preparation gave 0.2773 grm. AgBr.
- III. 0.5255 grm. substance gave 0.4142 grm.  $\text{CO}_2$  and 0.0734 grm.  $\text{H}_2\text{O}$ .
- IV. 0.3853 grm. of the same preparation gave 0.5731 grm. AgBr.

	I.	II.	III.	IV.
C	23.00		21.50	
H	1.77		1.55	
Br		58.53		63.30

These results showed merely that oxidation had taken place together with the substitution of hydrogen by bromine.

On boiling with bromine-water, total decomposition seemed to ensue, and no definite products could be isolated except oxalic acid and a small quantity of a volatile oil which had the odor of bromoform, and gave the characteristic odor of phenyl isocyanide when heated with anilin and alcoholic potash.

Although I have already carried on the investigation of pyroxanthin in several other directions, I have not as yet been able to study the reactions involved as much in detail as I could wish, and I must therefore reserve for a subsequent paper all description of these experiments.

Concerning the origin and mode of formation of the pyroxanthin, I can at present add nothing. Its high melting point, and its general behavior when compared with the properties of the oil from which it is made, lead directly to the conclusion that it results either from polymerization or condensation. Its formula,  $\text{C}_{15}\text{H}_{12}\text{O}_8$ , naturally suggests a trimolecular polymeric form; the composition of its bromine derivatives, on the other hand, favors rather the view that its molecule is the product of condensation.

Schweizer,\* in 1848, prepared from pyroligneous acid an oil to which he gave the name pyroxanthogen, as the substance from which the pyroxanthin was formed. He attempted no explanation of the mode of formation, and made no analysis of his product. Although

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\* Jour. pract. Chem., xliv. 129.

his description is not very precise, it is sufficient to show that it was a mixture tolerably complex in its nature.

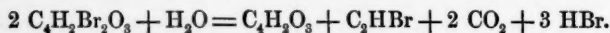
All my own attempts to isolate from the crude furfural the substance essential to the formation of the pyroxanthin have been unsuccessful. Its separation from the furfural is a matter of some difficulty, not only on account of the small quantities present, but also since it appears to be closely allied to furfural. In its boiling point or in its behavior towards reagents, I have as yet found no differences sufficiently well marked to form the basis for a method of separation.

For the present, at least, a more careful study of the pyroxanthin itself would seem to be the most speedy way to discover the mode of its formation.

#### MUCOBROMIC ACID.

Mucobromic acid was first made by Schmelz and Beilstein,\* in 1865, by the action of bromine and water upon pyromucic acid. They found its salts so unstable that they made little attempt to isolate them, but confined themselves chiefly to the study of the decomposition which ensued when it was boiled with alkalies, and of the reaction effected by argentic oxide.

They found that the acid was rapidly decomposed when boiled with baric hydrate, that bromacetylen was set free, and that baric carbonate was precipitated. In solution, they found, beside baric bromide, a sparingly soluble barium salt, to which they gave the name, baric muconate, and the formula,  $\text{BaC}_4\text{O}_8 \cdot \text{H}_2\text{O}$ . This formula was, however, based upon a single barium and two water determinations. They also prepared the free muconic acid, but made no further study of it than to establish the fact that it was a crystalline solid readily soluble in water, and that its lead salt was insoluble. They expressed the reaction which they supposed had taken place by the equation:—

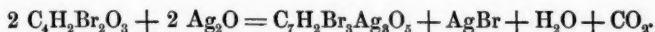


They also found that mucobromic acid was attacked when boiled with argentic oxide and water, that argentic bromide was formed, and at the same time a silver salt quite insoluble in water. This silver salt, according to their calculations of the analytical results which they obtained, had the formula  $\text{C}_7\text{H}_2\text{Br}_3\text{Ag}_5\text{O}_8$ , and they regarded this as an intermediate product standing between mucobromic and muconic acids. The acid was found to be a crystalline solid, which appeared to give

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\* Ann. Chem. u. Pharm., Suppl., iii. 276.

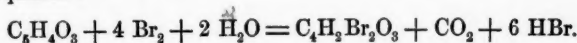
bromacetylen and muconic acid when heated with baric hydrate. The reaction with argentic oxide they wrote:—



In the course of the investigations upon mucic acid and its derivatives, which were begun in Limpricht's\* laboratory in 1868, mucobromic acid received more or less attention. Although it was found to be the only product when pyromucic acid was treated with water and an excess of bromine at ordinary pressures, Limpricht and Delbrück showed that it was completely decomposed when heated in a sealed tube to 120° with bromine and water, provided that three molecules of bromine, at least, were used to one of mucobromic acid. As products of the decomposition, they found, beside carbonic dioxide and hydrobromic acid, tribromethylenbromide,  $\text{C}_2\text{HBr}_3$ , perbromathylenbromide,  $\text{C}_2\text{Br}_6$ , tetrabrombutyric(?) acid,  $\text{C}_4\text{H}_4\text{Br}_4\text{O}_2$ , and dibromfumaric(?) acid,  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_4$ . The marks of interrogation appear in Limpricht's original paper. Limpricht and Lessing also found in one experiment that, by the reduction of mucobromic acid, a liquid was formed which boiled at about 120° and contained 84.8 per cent of carbon, 8.8 of hydrogen, and the remaining 6.4 per cent was oxygen. They were, however, unable to repeat the experiment with a like result.

In attempting the preparation of mucobromic acid, Mr. O. R. Jackson and I found that we were unable to obtain a satisfactory yield by following the method given by Schmelz and Beilstein or by Limpricht. Schmelz and Beilstein say that the quantity of water taken is not a matter of indifference, but neither they nor Limpricht make any specific statements as to the amount which they found to be most advantageous. They agree, however, that the bromine should be added slowly as long as it is taken up in the cold, that the solution should then be heated and bromine added as long as the color continues to disappear.

According to this method, we were unable to get more than 25 per cent of the theoretical yield; and at the same time we were obliged to use quite a large excess over the amount of bromine calculated from the equation:—




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\* Berichte d. deutsch. chem. Gesellsch., ii. 211; iii. 90, 671; iv. 805; Zeitschr. für Chem., 1869, 599; Ann. Chem. u. Pharm., clxv. 253.

We soon found that our yield was greatly increased and the excess of bromine proportionately decreased if the bromine was added rapidly. Later, when it was found that a low temperature was essential to the formation of mucochloric acid, the pyromucic acid and water were cooled with ice until the bromine had all been added, but the yield was not perceptibly affected.

We have obtained the best results by the following method: Pyromucic acid is suspended in ten times its weight of water contained in a flask fitted with reverse cooler and drop-funnel. The calculated amount of bromine is then rapidly added, cooling only so far as may be necessary to avoid loss of bromine. After the bromine is all added, the flask is heated, and the liquid kept boiling for ten or fifteen minutes. The solution may then be allowed to crystallize direct, although we have usually evaporated it until the hydrobromic acid began to volatilize in abundance before allowing it to cool. In either case the crystals should be well washed with cold water and recrystallized from boiling water. In this way we have found it easy to obtain 70 per cent and over of the theoretical yield.\*

The acid recovered from the mother liquors is usually very dark colored, and it cannot be purified by recrystallization from water either with or without the addition of bone-black. We have found, however, that such an acid may be obtained perfectly white by one or two recrystallizations from dilute sulphuric acid (1 : 4).

As to the properties of mucobromic acid, we can only confirm the statements of Schmelz and Beilstein. It crystallizes ordinarily from water in irregular leafy aggregates, from acid solutions or from certain other solvents in distinct rhombic plates. From a solution in concentrated hydrobromic acid, we have frequently obtained it in large compact crystals, with edges 10 to 12 mm. in length, but so striated as to render measurement impossible. It is sparingly soluble in cold water, very readily in hot water, in alcohol or in ether. In benzol or carbonic disulphide, it is very sparingly soluble in the cold, but dissolves quite readily on heating. Chloroform takes up a little when hot, most of which it deposits on cooling. In warm concentrated sulphuric acid, it dissolves freely, and, if not too strongly heated, crystallizes out on cooling or on dilution. It melts at 120–121°, and at a higher temperature it distills in part unchanged.

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\* Under conditions favorable to complete crystallization from the concentrated hydrobromic acid which forms the mother liquors, we have obtained 78 per cent.

The following analyses may serve to show the purity of the material used in the course of the following investigations:—

- I. 0.7840 grm. substance gave 0.5390 grm.  $\text{CO}_2$  and 0.0720 grm.  $\text{H}_2\text{O}$ .
- II. 0.9326 grm. substance gave 0.6340 grm.  $\text{CO}_2$  and 0.0712 grm.  $\text{H}_2\text{O}$ .
- III. 0.2347 grm. substance gave 0.3421 grm.  $\text{AgBr}$ .
- IV. 0.2331 grm. substance gave 0.3410 grm.  $\text{AgBr}$ .

Calculated for  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_8$ .

		I.	II.	Found. III.	IV.
C	18.60	18.75	18.55		
H	0.77	1.02	0.85		
Br	62.02			62.03	62.25

#### *Salts of Mucobromic Acid.*

Schmelz and Beilstein found that mucobromic acid decomposed baric carbonate, and that the barium salt thus formed was readily soluble in water, although it was decomposed during the spontaneous evaporation of the solution. As it seemed a matter of some interest to determine whether mucobromic acid was capable of forming salts, Mr. O. R. Jackson and I pursued the investigation one step further.

*Baric Mucobromate*,  $\text{Ba}(\text{C}_4\text{HBr}_2\text{O}_8)_2$ . We found that an aqueous solution of mucobromic acid dissolved baric carbonate readily, that the solution on standing soon turned brown, deposited a brownish flocculent precipitate, and contained then a baric bromide in abundance. On heating, the same change took place more rapidly, and when the solution was boiled a substance was volatilized with the steam which had a sharp, acrolein-like odor, and reduced silver oxide on heating. Although this change was rapid near  $100^\circ$ , we found that it was sufficiently slow at  $50\text{--}60^\circ$  to allow the preparation of a solution saturated at this temperature which on cooling with vigorous stirring deposited crystals of the barium salt. The mucobromic acid was suspended in very little water, the whole warmed to  $50\text{--}60^\circ$ , baric carbonate added in excess, and the solution filtered and cooled as rapidly as possible. Even with these precautions we found it difficult to saturate the acid completely without bringing about decided decomposition. The salt, therefore, usually contained more or less free acid, from which it could be completely freed by washing with ether. The salt when dried *in vacuo* over sulphuric acid hardly lost weight at  $100^\circ$ , but when heated a few degrees higher it turned



brown and gave out the sharp, penetrating odor mentioned above. Analyses I. and II. were made with a preparation crystallized from water without subsequent washing, III., IV., and V. with substance washed with ether.

- I. 0.9479 grm. gave 0.5018 grm.  $\text{CO}_2$  and 0.0547 grm.  $\text{H}_2\text{O}$ .
- II. 0.3434 grm. gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1165 grm.  $\text{BaSO}_4$ .
- III. 0.4186 grm. gave, on ignition, 0.1482 grm.  $\text{BaSO}_4$ .
- IV. 0.5747 grm. gave, on ignition, 0.2030 grm.  $\text{BaSO}_4$ .
- V. 0.7638 grm. gave, on ignition, 0.2695 grm.  $\text{BaSO}_4$ .

Calculated for $\text{Ba}(\text{C}_4\text{HBr}_2\text{O}_8)_2$ .			Found.			
		I.	II.	III.	IV.	V.
C	14.74	14.44				
H	0.30	0.63				
Ba	21.04		19.95	20.82	20.77	20.74

This salt is readily soluble even in the cold water, and soluble also in alcohol. On boiling its aqueous solution, the decomposition described above ensues, with the evolution of carbonic dioxide. This reaction has not yet been farther studied.

*Argentio Mucobromate*,  $\text{AgC}_4\text{HBr}_2\text{O}_8$ . The silver salt may be made by adding a concentrated solution of argentic nitrate to a solution of the barium salt. Since it is quite soluble even in cold water, it is better to use, instead of the barium, the calcium salt, in order to facilitate washing. It is precipitated in fine, felted needles, which blacken quite rapidly on exposure to diffused light, and are decomposed at once on moistening with alcohol or warming with water; argentic bromide is formed, together with some metallic silver. This substance was dried *in vacuo* for analysis:—

- I. 0.3601 grm. gave 0.1862 grm.  $\text{AgBr}$ .
- II. 0.5640 grm. gave 0.2903 grm.  $\text{AgBr}$ .

Calculated for $\text{AgC}_4\text{HBr}_2\text{O}_8$ .		Found.	
		I.	II.
Ag	29.59	29.70	29.56

*Ethyl Mucobromate*. The ethyl ether of mucobromic acid may readily be made by saturating its solution in absolute alcohol with hydrochloric acid, or more conveniently by warming this solution with concentrated sulphuric acid. If considerable sulphuric acid be used, the ether often crystallizes out on standing in large, well-formed crystals, otherwise it is precipitated by the addition of water and washed



with a dilute solution of sodic carbonate. The crude product contains impurities which can be removed only by repeated recrystallization from alcohol. This recrystallization is more conveniently accomplished if the moderately saturated solution is cooled to  $0^{\circ}$ . The ether crystallizes in large, transparent forms of the monoclinic system, which melt at  $50-51^{\circ}$  and boil at  $255-260^{\circ}$  with partial decomposition. When slightly warmed it has a pungent, aromatic odor.

The analysis of substance dried *in vacuo* over sulphuric acid gave:

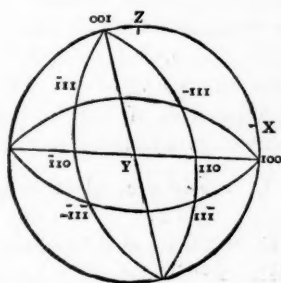
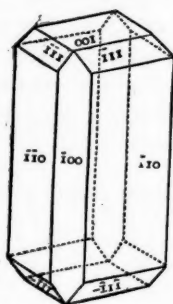
- I. 0.8583 grm. substance gave 0.7933 grm.  $\text{CO}_2$  and 0.1686 grm.  $\text{H}_2\text{O}$ .  
 II. 0.7000 grm. substance gave 0.6432 grm.  $\text{CO}_2$  and 0.1377 grm.  $\text{H}_2\text{O}$ .

Calculated for  $\text{C}_6\text{HBr}_3\text{O}_3 \cdot \text{C}_2\text{H}_5$ .

		Found.	
		I.	II
C	25.17	25.24	25.05
H	2.10	2.18	2.18

Mr. Mabery has studied the crystalline form of this substance, and obtained the following results:—

#### CRYSTALLINE FORM OF ETHYL MUCOBROMATE.



#### Monoclinic System.

Forms observed, —  $\{111\}$   $\{111\}$   $\{100\}$   $\{001\}$   $\{110\}$ .

$$a : b : c = 1.053 : 1 : 1.221 ; ac = 78^{\circ} 27'.$$

*Angles between Normals.*

	Found.	Calculated.
II1 : I11	82° 11'	Fundamental angles.
II0 : I10	92° 7'	
I11 : I10	32° 56'	
I11 : 001	64° 53'	64° 46'
I11 :-111	72° 11'	71° 50'
001 :-111	52° 44'	52° 53'
II0 :-111	29° 8'	29° 17'
I10 : I10	87° 50'	87° 53'
I10 : 001	81° 50'	82° 1'
I10 : 001	98° 4'	97° 59'
I10 : I00 *	45° 37'	46° 4'

*Action of Phosphoric Pentabromide and Acetylchloride.*

Mr. O. R. Jackson studied with me the behavior of mucobromic acid towards phosphoric pentabromide and acetylchloride.

*Mucobromylbromide.* When mucobromic acid is mixed with about four times its weight of phosphoric pentabromide, and the mixture heated for a short time at 110–115°, a quiet reaction sets in, the mass becomes liquid, and water then precipitates a heavy red oil, which after thorough washing with water gradually solidifies at ordinary temperatures, or immediately if cooled to 0°. This substance is very soluble in alcohol, ether, benzol, chloroform, or carbonic disulphide, but crystallizes well from a solution in a little hot alcohol when this is cooled to 0°. After repeated crystallization from alcohol, it forms small, slender prisms, which melt at 55–56°, and have the percentage composition corresponding to mucobromylbromide.

- I. 0.6643 grm. substance gave 0.3755 grm. CO<sub>2</sub> and 0.0374 grm. H<sub>2</sub>O.
- II. 0.2598 grm. substance gave 0.4573 grm. AgBr.
- III. 0.2252 grm. substance gave 0.3964 grm. AgBr.

Calculated for C<sub>4</sub>HBr<sub>5</sub>O<sub>3</sub>.

		I.	Found. II.	III.
C	14.96	15.41		
H	0.31	0.63		
Br	74.77		74.89	74.89

\* The form {100} was observed upon two or three individuals only, and the reflections were imperfect.

The behavior of this substance towards alkalies is especially characteristic. The reaction may best be observed when baric hydrate is cautiously added to a dilute alcoholic solution. An intense indigo-blue color is at once developed, which, however, soon passes through green to reddish yellow, with the simultaneous formation of a brown-red, flocculent precipitate. The same brown precipitate is formed when the mucobromylbromide is boiled in an excess of baric hydrate; but the two products which are most characteristic of the decomposition of mucobromic acid under the same conditions,\* bromacetylen and malonic acid, are formed in such small quantities that they may easily be overlooked. This peculiar behavior led us to suppose at first we had not the simple bromanhydride of mucobromic acid in our hands, but that an hydroxyl group outside the carboxyl had been replaced. A more careful study showed, however, that such was not the case. Although this mucobromylbromide is apparently little affected even by hot water, on boiling it is gradually decomposed, and the solution then contains mucobromic acid (m. pt. 120–121°). Absolute alcohol decomposes it with more difficulty; still, after several hours' boiling with reverse cooler, on evaporating the excess of alcohol and cooling strongly, crystals separated which had the characteristic form of the ethylmucobromate, and which melted at 51° after recrystallization from alcohol.

*Mucobromic Acetanhydride.* When mucobromic acid is heated in a sealed tube for several hours with an excess of acetylchloride at 120°, or when it is heated under ordinary pressure with acetic anhydride, a substance is formed, which is very soluble in alcohol, ether, or chloroform, and which may be purified by precipitation by water from its alcoholic solution. It falls as a colorless oil, which gradually solidifies in slender, dendritic needles, which melt at 53–54°.

0.9015 grm. gave 0.8050 grm. CO<sub>2</sub> and 0.1290 grm. H<sub>2</sub>O.

Calculated for C <sub>6</sub> HBr <sub>2</sub> O <sub>3</sub> · C <sub>2</sub> H <sub>3</sub> O.		Found.
C	24.00	24.36
H	1.33	1.59

That the acetyl group enters the carboxyl in this case is shown by the behavior of ethylmucobromate to acetylchloride. After several hours' heating, with an excess of acetylchloride, at 140–150°, the ether was found to be unaltered. The substance which was obtained crystallized in the form of the ethyl-ether, melted at 50°, and upon analysis proved to contain the required percentage of bromine.

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\* Cf. p. 188 *et seq.*

0.2720 grm. gave 0.3600 grm. AgBr.

Calculated for  $C_4HBr_3O_3 \cdot C_2H_2$ .

Br 55.94

Found.

56.32

*Action of Bromine.*

Limpricht and Delbrück studied in detail the action of bromine and water upon mucobromic acid, but they made no experiments with dry bromine. It therefore seemed advisable to investigate the action of dry bromine; since the reactions in this case would naturally be less complicated than with aqueous bromine, and on that account might prove to be of more service in determining the constitution of mucobromic acid. In my first experiments I employed equal molecules of bromine and mucobromic acid, but soon found that one molecule of bromine sufficed for the complete decomposition of nearly two molecules of mucobromic acid, although the products of the reaction were essentially the same whether the bromine was used in excess or not.

At 100°, very little action was noticeable; at 120–130°, the action was marked, but so slow that the temperature was raised to 140°. Here the reaction ran rapidly, and after two hours the bromine had disappeared. On cooling, the tubes were filled with long, prismatic crystals, which were permeated with a nearly colorless oil. On opening the tubes, hydrobromic acid gas escaped in abundance, and with it could be detected a comparatively small amount of carbonic dioxide. The partially solidified product of the reaction was treated with small quantities of cold water. The greater part of the prismatic crystals were in this way carried into solution; while the oil, in which a small quantity of crystals were yet to be seen, was left undissolved. This aqueous solution, upon evaporation, left a white, crystalline acid, very soluble in water, which for purification was converted into the barium salt. Before neutralizing the aqueous solution with baric carbonate, I found it best to evaporate to dryness, and take up a second time with a little cold water, in order to remove the small quantity of undecomposed mucobromic acid which often was present. The barium salt was precipitated several times from aqueous solution by alcohol, and finally crystallized from water by evaporation. Thus purified, it formed brilliant, transparent, rhombic plates, which lost water in desiccator slowly, but which I was unable to dehydrate perfectly by heat, either at ordinary pressures or *in vacuo*, without causing partial decomposition. The analysis of the air-dried salt gave percentages

required by a barium salt of dibrommaleic acid containing two molecules of water of crystallization.

- I. 0.8687 grm. of substance lost, at  $120^{\circ}$ , 0.0624 grm.  $\text{H}_2\text{O}$ . Of this dried salt, 0.4145 grm. gave, by ignition, 0.2341 grm.  $\text{BaSO}_4$ .
- II. 0.5780 grm. of air-dried salt gave, by ignition, 0.3010  $\text{BaSO}_4$ .

Calculated for  $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ .

		Found.	
		I.	II.
Ba	30.78	30.86	30.63
$\text{H}_2\text{O}$	8.09	7.07	

This salt is hardly more soluble in boiling water than in cold; in dilute alcohol, it is almost insoluble. The solubility in water was determined according to the method of V. Meyer.

- I. 7.1377 grm. of a solution saturated at  $19^{\circ}$  gave, on evaporation with  $\text{H}_2\text{SO}_4$  and ignition, 0.2296 grm.  $\text{BaSO}_4$ .
- II. 6.9649 grm. of a solution saturated at  $19^{\circ}$  gave 0.2249 grm.  $\text{BaSO}_4$ .

An aqueous solution saturated at  $19^{\circ}$ , therefore, contains of the anhydrous salt the percentages:—

I.	II.
5.65	5.67

The silver salt could best be made by the precipitation of a solution of the free acid by argentic nitrate. From dilute solution, it separated in long, flat needles; from concentrated solutions, it was precipitated in small prisms. It proved to be almost insoluble even in hot water. The dry salt exploded violently on heating, or by percussion.

0.6311 grm. of the salt, dissolved in dilute nitric acid, gave 0.4859 grm.  $\text{AgBr}$ .

Calculated for  $\text{Ag}_5\text{C}_4\text{Br}_2\text{O}_4$ .

	Found.
Ag	44.27
	44.22

The lead salt fell as a crystalline precipitate upon the addition of plumbic acetate even to a dilute solution of the free acid.

The acid was liberated from the pure barium salt by the addition of normal sulphuric acid, in quantity insufficient for complete precipitation; the aqueous solution was allowed to evaporate spontaneously; and the acid was then separated from the excess of barium salt by means of ether free from alcohol. Prepared in this way, the acid formed a

mass of indistinct, aggregated needles, extremely soluble in water, ether, or alcohol; and almost insoluble in boiling chloroform, benzol, ligroin, or carbonic disulphide. From a mixture of ether and chloroform, it could be crystallized in the form of fine, felted needles.

After standing in desiccator, the acid gave on analysis too high a percentage of bromine (I.). It was therefore washed with chloroform, the excess of chloroform evaporated in a paraffine desiccator according to Liebermann's suggestion; but the percentage of bromine remained essentially unaltered (II.). I therefore dissolved the acid in hot water, allowed the solution to evaporate spontaneously, and dried by exposure to the air alone, but failed to alter its composition (III.). Subsequently I dissolved the pure anhydride described below in hot water, and found that the acid obtained by spontaneous evaporation of this solution when air-dried also contained more bromine than the formula of the acid required (IV.).

- I. 0.2050 grm. substance gave 0.2860 grm. AgBr.
- II. 0.2305 grm. substance gave 0.3200 grm. AgBr.
- III. 0.2150 grm. substance gave 0.3000 grm. AgBr.
- IV. 0.2500 grm. substance gave 0.3475 grm. AgBr.

Calculated for  $C_6H_5Br_3O_4$ .

		Found.			
		I.	II.	III.	IV.
Br	58.38	59.37	59.08	59.38	59.15

From these experiments it would appear that the acid, even at ordinary temperatures, is partially converted into its anhydride. This change goes on rapidly at temperatures near  $100^\circ$ , so that it is impossible to obtain constant melting points. The preparations analyzed melted at  $120$ – $125^\circ$  when warmed with ordinary rapidity. The acid was but slightly volatile with steam, but could be distilled with greatest readiness with the vapor of concentrated hydrobromic acid.

From this acid the anhydride could be obtained without difficulty in a pure state, by heating to  $120^\circ$  in a current of dry carbonic dioxide. The sublimation began at  $100^\circ$ , or possibly lower, but became rapid at  $115$ – $120^\circ$ . The anhydride condensed in lustrous, flattened needles, which melted at  $114$ – $115^\circ$ . In cold water it dissolved but slowly; in alcohol, ether, benzol, ligroin, chloroform, or carbonic disulphide, it was readily soluble.

- I. 0.3672 grm. gave 0.2510 grm.  $CO_2$  and 0.0010 grm.  $H_2O$ .
- II. 0.2680 grm. gave 0.3870 grm. AgBr.

Calculated for $C_4Br_2O_4$ .		Found.	
		I.	II.
C	18.75	18.65	
H	—	0.02	
Br	62.50		62.61

The aqueous solution obtained by treating the original product from the action of bromine with cold water, therefore, contained mainly an acid of the composition of dibrommaleic acid.

In the mother liquors from the baric dibrommaleate there appeared to be a trace of a more soluble barium salt beside baric bromide; but its quantity was too small to admit of separation and analysis.

The oily residue left undissolved by water gradually solidified upon standing. Cold chloroform dissolved the greater portion of it, leaving a small quantity of short, prismatic crystals. Upon evaporation of the chloroform, an oil was left, which gradually solidified in masses of radiated prisms, contaminated with a small quantity of an oily impurity whose nature could not further be determined. After several crystallizations from alcohol, this substance melted at 55–56°, and when treated with baric hydrate gave the characteristic reactions of mucobromylbromide. It was still further identified by analysis.

0.2280 grm. substance gave 4000 grm. AgBr.

Calculated for $C_4HBr_2O_4$ .		Found.
Br	74.77	74.68

The prismatic crystals, which were sparingly soluble in cold water and chloroform, were recrystallized from hot water, and showed then the characteristic properties of ordinary dibromsuccinic acid. On heating, they remained unaltered till the temperature had risen to over 200°; at a somewhat higher point, they had completely volatilized. The sublimate condensed in the colder portions of the tube in oil drops, which gradually solidified. The melting point of the solid thus obtained, after pressing with filter paper, was found to be 126°. According to Fittig and Petri,† the sublimate formed under the same conditions from dibromsuccinic acid has the melting point of monobrommaleic acid (128°). The quantity of dibromsuccinic acid formed in this reaction was quite small.

0.2855 grm. substance gave 0.3880 grm. AgBr.

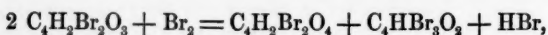
Calculated for $C_4H_2Br_2O_4$ .		Found.
	57.97	57.83

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† Ann. Chem. u. Pharm., excv. 58.

When the original product of the reaction was treated at once with dry chloroform, the greater part was instantly carried into solution; and the dibromsuccinic acid, together with a small quantity of mucobromic acid, were left undissolved. The filtered chloroform solution, when shaken with a few drops of water, gradually solidified with separating crystals of dibrommaleic acid; so that the original product must have contained the dibrommaleic acid as anhydride.

The two main products of the reaction were, therefore, dibrommaleic anhydride and mucobromylbromide. The relative weights of these two products were such as to suggest at once the equation:—



when the dibrommaleic acid would readily pass into its anhydride. The weights obtained in successive preparations were, however, found to vary so much that I am inclined to consider the anhydride as the direct product of the reaction, and the mucobromylbromide a secondary product formed by the action of the hydrobromic acid set free. In either case, the formation of dibromsuccinic acid can hardly be explained without assuming a reducing action of the hydrobromic acid, like that which is normal to hydriodic acid. Although reductions of this sort by the action of hydrobromic acid have seldom been noticed, the conversion of tartaric acid into monobromsuccinic acid by this means, noticed by Kekulé\* in 1864, would seem to be perfectly analogous.

#### *Dibrommaleic Acid of Kekulé.*

In 1864 Kekulé† found among the products of the action of bromine and water upon succinic acid an acid,  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_4$ , to which he gave the name dibrommaleic acid. It formed white, clustered needles, which were extremely soluble in water, alcohol, or ether, and melted at  $112^\circ$ ; at higher temperatures the acid distilled apparently unchanged, and it volatilized readily with steam. For the further characterization of the acid, Kekulé made the silver and lead salts. The silver salt could be precipitated from an aqueous solution of the acid, by the addition of argentic nitrate; and, according to the concentration of the solution, it appeared as a granular, crystalline precipitate, or in slender, glistening needles. The dry salt exploded violently by heat or percussion. The lead salt was thrown down by the

\* Ann. Chem. u. Pharm., cxxx. 30.

† Ann. Chem. u. Pharm., cxxx. 1.



addition of plumbic acetate to an aqueous solution of the acid, and when air-dried it was found to contain a molecule of water.

Since its discovery by Kekulé, the acid prepared in this way has been mentioned but twice, as far as I know; and these notices contain no additional facts which could serve to assist in its identification. Bourgoin\* gives its melting point as  $110^{\circ}$ , and asserts that it distills unaltered. Fittig and Petri,† in their attempts to prepare the tribromsuccinic acid, which had been described by Bourgoin, obtained dibromsuccinic acid and a substance crystallizing in hemispherical aggregations, which, from their melting point ( $112^{\circ}$ ) and volatility with steam, they recognized as dibrommaleic acid.

In 1873 Limpricht and Delbrück‡ described an acid of the same composition, which they made by the action of bromine and water upon mucobromic acid. They found it difficult of purification; and, in their study of it, they were to all appearance hampered by lack of material. The acid melted at  $108-120^{\circ}$ , and by sublimation it was converted into its anhydride,  $C_4Br_2O_3$ , which melted at  $95-120^{\circ}$ . The barium salt they obtained in colorless, tabular crystals, to which they assigned the formula,  $BaC_4Br_2O_4 \cdot 2H_2O$ . The silver salt they found to be insoluble; but it did not explode either by heat or percussion. They assumed, apparently without hesitation, that this acid was isomeric with that of Kekulé, and therefore named it dibromfumaric acid.

The acid made by the action of bromine upon mucobromic acid, which I have just described, agreed in most respects closely with the acid described by Kekulé; and yet the higher melting point and the ready formation of the anhydride rendered a further comparison necessary in order to settle the question of identity.

In the preparation of dibrommaleic acid, I followed in general the method of Kekulé; but, since this was to be the main product of the reaction, I was obliged to use a greater proportion of bromine and water, in order to get any considerable yield.

I obtained good results by using to one part of succinic acid two of water and four of bromine, and heating twenty hours at  $140^{\circ}$ . The mother liquors from which the greater part of the dibromsuccinic acid had been separated were distilled, the distillate neutralized with baric carbonate, and the baric dibrommaleate precipitated from the filtered

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\* Bull. Soc. Chim. [2], xxi. 404; xxii. 443.

† Ann. Chem. u. Pharm., cxcv. 76.

‡ Ann. Chem. u. Pharm., clxv. 204.

solution. After several precipitations from aqueous solution by alcohol, it was crystallized from water by evaporation, and dried by exposure to the air. The salt could not be distinguished in outward appearance from that made from mucobromic acid.

- I. 2.4931 grm. of air-dried salt lost in weight, at 125–130°, 0.2136 grm. 0.7670 grm. of this dried salt gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.4393 grm.  $\text{BaSO}_4$ .  
 II. 0.5899 grm. air-dried salt gave 0.3102 grm.  $\text{BaSO}_4$ .

Calculated for  $\text{C}_6\text{H}_7\text{Br}_3\text{O}_4\cdot\text{Ba}\cdot 2\text{H}_2\text{O}$ .

		Found.	
		I.	II.
Ba	30.78	30.79	30.91
$\text{H}_2\text{O}$	8.09	8.15	

The solubility of this salt was determined according to the method of V. Meyer.

8.9481 grm. of a solution saturated at 20° gave 0.2912 grm.  $\text{BaSO}_4$ .

The aqueous solution saturated at 20°, therefore, contains 5.71 per cent of the anhydrous salt.

From this barium salt, the free acid was made in the manner above described. In its behavior towards solvents, it resembled perfectly the acid made from mucobromic acid, and it melted between 120° and 123°. This acid I did not analyze; but the analyses published by Kekulé show too high a percentage of bromine, and in this respect do not differ essentially from those I have given above.

Calculated for  $\text{C}_6\text{H}_7\text{Br}_3\text{O}_4$ .

Br. 58.38

Found by Kekulé.

I.	II.
58.98	59.08

By heating this acid in a stream of carbonic dioxide, the anhydride could readily be made in appearance and behavior perfectly identical with the compound already described, and melting at 114°–115°.

- I. 0.4160 grm. substance gave 0.2860 gr.  $\text{CO}_2$  and 0.0032 grm.  $\text{H}_2\text{O}$ .  
 II. 0.2840 grm. substance gave 0.4165 grm.  $\text{AgBr}$ .

Calculated for  $\text{C}_6\text{Br}_3\text{O}_2$ .

C	18.75
H	—
Br	62.50

Found.

I.	II.
18.75	
0.10	
	62.34

The identity of the dibrommaleic acids made by the action of dry bromine upon mucobromic acid and aqueous bromine upon succinic is thus sufficiently established. They each give an anhydride melting at  $114-115^{\circ}$ ; their barium salts have the same composition,  $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ; and the solubility of these two salts in water is the same, the saturated aqueous solution containing in one case 5.66 per cent of the anhydrous salt at  $19^{\circ}$ , in the other 5.71 per cent at  $20^{\circ}$ .

Although I have several times tried the action of bromine and water upon mucobromic acid, according to the method of Limpricht and Delbrück, I have not as yet submitted the product obtained in this way to any very extended investigation. In all qualitative reactions it is identical with the acid I have described; and, considering the mode of its formation, one can hardly doubt its identity. Moreover, with regard to the slight differences which would seem to have induced Limpricht and Delbrück to consider their acid isomeric with Kekulé's, I have been unable to confirm their observations. The melting point ( $95-120^{\circ}$ ) given by them for the anhydride does not give confidence in the purity of their material. The higher percentage of barium (31.9) \* which they found in their barium salt would be in no way at variance with my results, even if its purity were granted, since the material they analyzed had been dried *in vacuo* (over sulphuric acid?), and my own experiments have shown that it slowly effloresces under these conditions.

Although the foregoing facts seemed to warrant the conclusion that the dibrommaleic acid of Kekulé belonged to the maleic series, inasmuch as the anhydride was the direct product of the reaction of bromine upon mucobromic acid, still I thought it advisable to prove this directly, more especially since all analogy pointed to the formation of a derivative of fumaric acid under the conditions essential to its preparation from succinic acid. I therefore dissolved in water the pure anhydride prepared from succinic acid, neutralized the solution with baric carbonate, precipitated the barium salt by alcohol, and recrystallized it from water. This salt proved to be identical with that which was obtained directly from the acid.

0.7525 grm. of the air-dried salt lost on heating to about  $120^{\circ}$  0.0581 grm.; 0.6933 grm. of this dried salt gave 0.3922 grm.  $\text{BaSO}_4$ .

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\* Limpricht and Delbrück erroneously calculated the percentage of barium in the salt  $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  as 31.9 per cent, instead of 30.78, and therefore gave the same formula.

Calculated for $\text{BaC}_2\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .		Found.
Ba	30.78	30.69
$\text{H}_2\text{O}$	8.09	7.72

The solubility was also determined by the method of V. Meyer.

7.6833 grm. of the solution saturated at  $19^\circ.5$  gave, on evaporation with  $\text{H}_2\text{SO}_4$  and ignition, 0.2446 grm.  $\text{BaSO}_4$ .

An aqueous solution saturated at  $19^\circ.5$  contained therefore 5.58 per cent of the anhydrous salt.

This proves that dibrommaleic acid may be carried unchanged through its anhydride, and that it consequently belongs to the maleic series, unless, indeed, its behavior is radically changed by the complete replacement of its hydrogen by bromine. That such is not the case has recently been shown by Bandrowski,\* who has discovered an acid of the same composition, which is undoubtedly dibromfumaric acid. This acid melts at  $219\text{--}220^\circ$ , and by distillation is converted into dibrommaleic acid.

#### *Mucobromic Acid with Oxidizing Agents.*

The close connection between mucobromic acid and dibrommaleic, as shown by its behavior when heated with bromine, naturally suggested the direct conversion of the one into the other by oxidation.

An aqueous solution of chromic acid does not act upon mucobromic acid at ordinary temperatures, even after standing for weeks. On warming, carbonic acid is freely given off, and at the same time a sharp, acrolein-like odor is noticed. If one atom of oxygen is employed for every molecule of mucobromic acid, a portion of the mucobromic acid seems to be completely destroyed, while nearly one half of it remains unaltered, and may be extracted with ether after the reaction is completed. When two atoms of oxygen are taken, but little mucobromic acid escapes oxidation; but I have been unable to isolate well-marked products of the reaction, in any considerable quantities. When the solution is distilled, the substance possessing the sharp, pungent odor passes over with the steam. It is quite soluble in water, although not in all proportions, and its aqueous solution reduces silver energetically from the oxide even in the cold. Although this is the most striking product of the oxidation, it is formed in such small quantities that I have as yet been unable to study it further. After

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\* Berichte der deutsch. chem. Gesellsch., xii. 2213.

this volatile product has been distilled off, but a trace of organic acid can be extracted from the retort residue by ether. This acid is chiefly mucobromic; but with it I have found dibrommaleic acid in quantity barely sufficient for the recognition of its barium salt under the microscope when precipitated from aqueous solution by alcohol. The oxidation with nitric acid gives somewhat better results. When mucobromic acid is boiled with ten times its weight of nitric acid of sp. gr. 1.20, carbonic dioxide is slowly given off, the escaping gas renders a solution of argentic nitrate turbid, and yet, if the heat is continued for several hours, a considerable portion of the mucobromic acid is found to be converted into dibrommaleic acid. In one experiment I obtained, after several hours' boiling, from 5 grm. of mucobromic acid 2.3 grm. of baric dibrommaleate and 1.5 grm. of unaltered mucobromic acid. This corresponds to nearly forty per cent of the theoretical yield of dibrommaleic acid from the mucobromic acid which entered into the reaction. Stronger nitric acid oxidizes more rapidly, but the yield of dibrommaleic acid is smaller; if much more dilute acid is used, the mucobromic acid is hardly altered.

Precisely the same effect is produced by long boiling with bromine water, carbonic dioxide being evolved as before, and the yield of dibrommaleic acid remaining essentially the same. The identity of the acid made by bromine water was established by the analysis of the barium salt. This salt was precipitated several times from aqueous solution by alcohol, recrystallized from water, and contained then the required percentage of barium.

0.5493 grm. of the air-dried salt gave 0.2887 grm.  $\text{BaSO}_4$ .

Calculated for  $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

Ba 30.78

Found.

30.90

Limpricht found that mucobromic acid was the only product when pyromucic acid suspended in water was treated with an excess of bromine at ordinary pressures. Since mucobromic acid is itself converted into dibrommaleic acid by boiling it with bromine water, it follows that the latter acid must of necessity be formed in the preparation of mucobromic acid. For its detection, the mother liquors, from which the mucobromic acid had been separated as completely as possible, were distilled. The distillate, consisting chiefly of concentrated hydrobromic acid (b. pt.  $126^\circ$ ) was partially neutralized with potassic carbonate, and thoroughly shaken out with ether. The residue left on evaporation of the ether was taken up with water, and the acid solution saturated with baric carbonate. Alcohol precipitated from

the filtered solution baric dibrommaleate in characteristic form. For analysis, the salt was recrystallized from water, and dried by exposure to the air.

0.4709 grm. of this salt gave 0.2516 grm.  $\text{BaSO}_4$ .

Calculated for $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .		Found.
Ba	30.78	31.41

Since the percentage of barium was found to be too high, for further identification the acid was set free, and converted into the anhydride by sublimation. This crystallized in the characteristic flattened needles, which melted at  $114^\circ$ . The quantity of dibrommaleic acid formed in the ordinary preparation of mucobromic acid is very considerable, and amounted in one case to about one per cent of the pyromucic acid employed. The quantity must, however, of necessity be very variable.

The oxidation of mucobromic acid by means of argentic oxide was investigated by Schmelz and Beilstein. They gave to the chief product of the reaction the formula,  $\text{Ag}_3\text{C}_7\text{H}_2\text{Br}_3\text{O}_5$ ; but it is evident from an inspection of their analyses that they had in their hands the silver salt of dibrommaleic acid in a nearly pure condition.

	Calculated		Found by Schmelz and Beilstein.					
	for $\text{Ag}_3\text{C}_7\text{H}_2\text{Br}_3\text{O}_5$ .	for $\text{Ag}_3\text{C}_4\text{Br}_2\text{O}_4$ .	I.	II.	III.	IV.	V.	VI.
C	11.51	9.84	10.07	10.64	11.30			
H	0.27	—	0.64	0.37	0.32			
Br	32.87	32.78				32.47		
Ag	44.38	44.27					44.25	44.26

With this close agreement between the observed and calculated percentages, I did not consider it worth while to analyze, myself, this silver salt. Still it was evidently necessary to prepare from it the barium salt in order to compare this with the product I had already studied.

Since argentic bromide is readily formed when the silver salt of mucobromic acid is heated with water, I added at once an excess of argentic oxide to a warm solution of mucobromic acid, and heated it quickly to the boiling point. The oxidation seemed to be more neatly accomplished in this way than by the gradual addition of the argentic oxide, although even then there was formed a considerable quantity of argentic bromide. After the action had ceased, the whole was acidified with hydrochloric acid, and the filtered solution shaken out with ether. The acid left upon evaporation of the ether was then taken up with water, neutralized with baric carbonate, and the barium salt purified as

before. An analysis of the air-dried salt, and a determination of its solubility, proved that the acid was identical with that made by the action of bromine upon succinic or mucobromic acid.

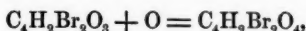
0.5225 grm. of the air-dried salt gave 0.2741 grm.  $\text{BaSO}_4$ .

Calculated for $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .		Found.
Ba	30.78	30.84

9.2092 grm. of an aqueous solution saturated at  $18^\circ.5$  according to the method of V. Meyer, gave on evaporation with  $\text{H}_2\text{SO}_4$  and ignition 0.2944 grm.  $\text{BaSO}_4$ .

According to this determination, an aqueous solution saturated at  $18^\circ.5$  contains 5.61 per cent of the anhydrous salt.

This oxidation of mucobromic acid by means of argentic oxide into dibrommaleic acid,



would seem to show conclusively that it is the half aldehyde of the dibasic dibrommaleic acid.

#### *Decomposition by Heat.*

If mucobromic acid is quickly heated, the greater part of it distils unchanged; but, if the temperature is so regulated that it can distil but slowly, a great part of it suffers decomposition. The reaction which it undergoes I have, as yet, studied only so far as to prove that dibrommaleic acid is one of the chief products. If the acid is mixed with sand and slowly distilled, streams of hydrobromic acid and carbonic dioxide are given off, and a colorless oil passes over, which, on standing, partially solidifies. On the addition of water, the solid portion dissolves, leaving an oil which is volatile with steam, and is not wholly insoluble in water. Its aqueous solution reduces argentic oxide, and possesses an intolerably sharp, pungent odor. In the investigation of this oil, I have not yet obtained definite results.

The aqueous solution contained dibrommaleic acid, which was identified by an analysis of its barium salt. The solution of the barium salt obtained, at first was highly colored, and from it pure material could be made only by repeated precipitation from aqueous solution with the smallest possible quantity of alcohol. In this way, a perfectly colorless salt was made, and it was then recrystallized from water.

0.6652 grm. of the air-dried salt gave 0.3498 grm.  $\text{BaSO}_4$ .



Calculated for  $\text{BaC}_4\text{Br}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ .

Found.

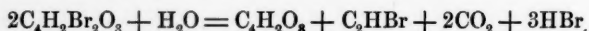
Ba 30.78

30.91

The amount of dibrommaleic acid thus formed is about 15 per cent of the mucobromic acid taken, and 30 per cent of the total weight of the distillate.

*Action of Baric Hydrate.*

The action of baric hydrate upon mucobromic acid was first studied by Schmelz and Beilstein. The results they obtained were extremely interesting, but needed extension in several directions. More especially inviting was the muconic acid which they considered formed in the reaction, and to which they gave the formula  $\text{H}_2\text{C}_4\text{O}_8$ . In beginning this investigation, Mr. O. R. Jackson and I thought it best at the outset to test experimentally the truth of the equation,



which Schmelz and Beilstein had given as an expression of the reaction, and at the same time to determine the conditions most favorable to the formation of baric muconate. The qualitative results we found to be precisely in accordance with their statements, and it was only necessary to study the reaction quantitatively. A weighed quantity of mucobromic acid was introduced into a flask fitted with reverse cooler, and dissolved in a little warm water. The upper end of the cooler was then connected with a series of wash-bottles which were filled with an ammoniacal solution of cuprous oxide, made by reducing an ammoniacal solution of pure cupric sulphate with metallic copper. The air in the apparatus was then displaced by pure hydrogen, a measured quantity of a standard solution of baric hydrate introduced into the flask, and heat applied. When the action appeared to be finished, we determined the weight of the baric carbonate which had been formed in the reaction, the weight of the baric carbonate which could be precipitated from the filtered solution by carbonic dioxide, and the weight of the baric muconate left on evaporation after washing out the baric bromide with cold water. In order to determine the amount of bromacetylen, we filtered off the voluminous precipitate of acetylen copper which had separated in the wash-bottles, acidified the filtrate, and precipitated the bromine with argentic nitrate.

The results which we obtained are given in the following table; in each case 2 grm. of mucobromic acid were taken.



No	BaO <sub>3</sub> H <sub>2</sub> taken.	BaCO <sub>3</sub> by CO <sub>2</sub> .	Br.	BaCO <sub>3</sub> formed.	"Baric muconate."
I.	1.994		0.372	0.57	
V.	2.971	trace	0.293	1.07	0.40
VI.	2.971	trace	0.333	1.05	0.55
II.	5.988	3.52	0.135	0.54	0.85
III.	5.942	3.25	0.146	0.50	0.87
IV.	5.942	3.40	0.128	0.53	0.97
VII.	8.044	5.75	0.135	0.47	0.95
VIII.	8.044	5.90	0.112	0.35	0.90

In order to compare these results more conveniently, we calculated from them the corresponding molecular ratios.

The following table contains the number of molecules of baric hydrate which we used in the various experiments for the decomposition of one molecule of mucobromic acid, the number of molecules of baric hydrate which actually entered into the reaction, and the fractions of a molecule of bromacetylen, carbonic dioxide, and baric muconate which were formed in each case. In accordance with the results which we afterwards obtained, the muconate is here calculated as baric malonate.

No.	Baric hydrate.		Bromacetylen.	Carbonic dioxide.	"Baric muconate."
	taken.	used.			
I.	1.50	1.50	0.60	0.37	
V.	2.24	2.24	0.47	0.70	0.20
VI.	2.24	2.24	0.54	0.69	0.28
II.	4.51	2.21	0.22	0.35	0.43
III.	4.48	2.35	0.24	0.33	0.44
IV.	4.48	2.25	0.21	0.35	0.49
VII.	6.07	2.30	0.22	0.31	0.48
VIII.	6.07	2.17	0.18	0.23	0.45

These results were sufficient to show that, in the decomposition by baric hydrate, we had to deal with at least two independent reactions; that one of these reactions led to the formation of carbonic dioxide and bromacetylen, while the second had for its chief product the sparingly soluble barium salt, — the baric muconate of Schmelz and Beilstein. Moreover, it was evident that, in order to obtain the best yield of the latter salt, a large excess of baric hydrate should be employed.

In the preparation of the sparingly soluble barium salt, we used five or six molecules of baric hydrate to one of mucobromic acid. When the reaction appeared at an end, we precipitated the excess of baric hydrate with carbonic dioxide, and evaporated the filtered solution to a small volume. When this solution was slowly evaporated upon the water bath, we found, in accordance with the statements of Schmelz and Beilstein, that the salt separated in thin crusts which had no visible crystalline structure. If, however, the solution was boiled down rapidly over the lamp, at a certain point the salt suddenly separated in fine, silky needles, which were still further increased as the solution cooled. These crystals were well washed with cold water, redissolved in boiling water, and precipitated with plumbic acetate. In this way a granular lead salt was thrown down, which, when examined under the microscope, was seen to consist of well-formed rhombic plates. For analysis, the salt was dried at  $110^{\circ}$ .

I. 0.5939 grm. substance gave 0.2434 grm.  $\text{CO}_2$  and 0.0470 grm. of  $\text{H}_2\text{O}$ .

II. 0.3459 grm. gave, by ignition with  $\text{H}_2\text{SO}_4$ , 0.3402 grm.  $\text{PbSO}_4$ .

	Calculated for $\text{PbC}_6\text{O}_6$	Calculated for $\text{PbC}_6\text{H}_2\text{O}_6$	Found.	
			I.	II.
C	15.84	11.65	11.18	
H	—	0.65	0.88	
Pb	68.32	66.99		67.22

It will be seen that the percentages found correspond closely with those required by plumbic malonate, and differ widely from those required by the formula of Schmelz and Beilstein.

The barium salt also agrees well with the description of baric malonate given by Heintzel\* and Finkelstein.† The analyses we have made of the salt have given us too high a percentage of barium, although materially lower than that found by Schmelz and Beilstein.

I. 0.5212 grm. of the salt, dried at  $120^{\circ}$ , gave 0.5214 grm.  $\text{BaSO}_4$ .

II. 0.3455 grm. of the salt, dried at  $100^{\circ}$ , gave 0.3159 grm.  $\text{BaSO}_4$ .

III. 0.2139 grm. of the salt, dried at  $100^{\circ}$ , gave 0.1956 grm.  $\text{BaSO}_4$ .

	Calculated for $\text{BaC}_6\text{H}_2\text{O}_6 \cdot \text{H}_2\text{O}$	Found.			
		I.	II.	III.	Schmelz and Beilstein
Ba	53.33	54.70	53.75	53.73	56.32

\* Ann. Chem. u. Pharm., cxxix. 133.

† Ann. Chem. u. Pharm., cxxxiii. 343.

The result of Schmelz and Beilstein is here calculated for the hydrous salt. They found that the salt, when dried at  $100^{\circ}$ , lost 4.15 per cent of water at  $200^{\circ}$ , and contained then 58.6 per cent of barium.

From the lead salt we made the free acid by means of hydric sulphide, and found it very soluble in water or alcohol, less freely in ether. From aqueous solution it crystallized in irregular rhombic plates, occasionally in more compact prismatic forms. After several recrystallizations from water, and thorough drying over sulphuric acid, these crystals melted at  $131.5$ – $132^{\circ}$ . This agrees with the melting point of malonic acid, as given by Heintzel, although it is somewhat lower than that more recently given by Pinner.\* A combustion left no doubt of the identity and the purity of the acid.

0.3849 grm. substance gave 0.4871 grm.  $\text{CO}_2$  and 0.1395 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_3\text{H}_4\text{O}_4$ .	Found.
C	34.61	34.51
H	3.85	4.03

The quantity of baric malonate which we obtained from mucobromic acid agreed with the results of our experiments upon a smaller scale, and amounted to nearly 50 per cent of the theoretical yield. The mother liquors contained, beside baric bromide, baric formiate, whose presence could readily be established by qualitative tests.

Although the gaseous product formed by this decomposition with baric hydrate agreed closely in its qualitative reactions with bromacetylen, it seemed to us advisable to prove its identity a little more rigorously. We therefore passed the gas, diluted with hydrogen, into bromine and water. The crystalline solid which resulted we washed with dilute sodic hydrate, then with water, and finally recrystallized it from alcohol. Thus purified, it formed long, brilliant prisms, which melted at  $54^{\circ}$ . The melting point of pentabromethan is given by Lennox † as  $48^{\circ}$ ; by Reboul, ‡  $48$ – $50^{\circ}$ ; by Limpricht and Delbrück, §  $50$ – $52^{\circ}$ ; and by Bourgoin, ||  $56$ – $57^{\circ}$ . The prismatic angle could readily be determined, and the measurement of several individuals

\* Berichte der deutsch. chem. Gesellsch., viii. 965.

† Lond. R. Soc. Proc., xi. 267; Ann. Chem. u. Pharm., cxxii. 122.

‡ C. R., liv. 1229; Ann. Chem. u. Pharm., cxxiv. 267; Bull. Soc. Chim., 1862, 75.

§ Ann. Chem. u. Pharm., clxv. 297.

|| Ann. Chim. Phys. [5], iv. 423; Bull. Soc. Chim. [2], xxiii. 175, 257.

gave as its mean value  $104^{\circ} 17'$ . Reboul gives the same angle in crystals of pentabromethan as  $104^{\circ} 20'$ , and Bourgoin as  $104^{\circ} 16'$ .

The identity of the substance was still further established by analysis.

0.1151 grm. substance gave 0.2547 grm. AgBr.

Calculated for $C_3HBr_5O_2$ .		Found.
Br	94.12	94.17

After we had proved that malonic acid was one of the final products of the decomposition of mucobromic acid when boiled with an excess of baric hydrate, we attempted, by various modifications of the mode of decomposition, to isolate intermediate products, which might give us information concerning the nature of the reaction. After many unsuccessful experiments, we found that such products resulted from the action of alkalies at ordinary temperatures, and they were most conveniently studied when baric hydrate was employed.

*Baric Dibromacrylate*,  $Ba(C_3HBr_2O_2)_2$ . If mucobromic acid is gradually added to a solution of baric hydrate containing a large excess of baric hydrate in suspension, it dissolves readily, and the crystals of baric hydrate at the same time gradually disappear. After a while a beautifully crystalline barium salt begins to separate, the amount of which increases rapidly as the acid is added. In order to prepare this salt, we found it best to add the mucobromic acid until one molecule had been used for every one and a half molecules of baric hydrate. At first we used two parts of crystallized baric hydrate and four of water to one part of mucobromic acid, but subsequently we reduced the amount of water one half. After the necessary amount of mucobromic acid had been added in small portions, care being taken to prevent any elevation of temperature, the whole was allowed to stand for a short time, and the crystals which had separated were then filtered off on the pump. These were washed with a little cold water, exposed to carbonic dioxide until neutral in their reaction, and then recrystallized from water or diluted alcohol. From alcohol, the salt crystallized in pearly rhombic plates; from water, in irregular leafy forms, or, on slow evaporation, in massive aggregates of rhombic plates. When dried by exposure to the air, they lost nothing over sulphuric acid or when heated to  $80^{\circ}$ . At  $100^{\circ}$  they slowly lost in weight.

The air-dried salt gave on analysis the percentages required by the barium salt of a dibromacrylic acid.

- I. 1.0621 grm. of the salt gave 0.4745 grm.  $\text{CO}_2$  and 0.0780 grm.  $\text{H}_2\text{O}$ .  
 II. 1.0363 grm. of the salt gave 0.4609 grm.  $\text{CO}_2$  and 0.0743 grm.  $\text{H}_2\text{O}$ .  
 III. 0.6187 grm. gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.2415 grm.  $\text{BaSO}_4$ .  
 IV. 0.6180 grm. gave 0.2434 grm.  $\text{BaSO}_4$ .  
 V. 0.5785 grm. gave 0.2269 grm.  $\text{BaSO}_4$ .  
 VI. 0.3522 grm. gave 0.1381 grm.  $\text{BaSO}_4$ .

Calculated for  $\text{Ba}(\text{C}_8\text{HBr}_2\text{O}_2)_2$ .

		I.	II.	Found.	III.	IV.	V.	VI.
C	12.10	12.19	12.14					
H	0.34	0.82	0.80					
Ba	23.03			22.95	23.15	23.05	23.05	

*Argentio Dibromacrylate*,  $\text{AgC}_8\text{HBr}_2\text{O}_2$ . From the barium salt, or, better, from a solution of the free acid, the silver salt was made by the addition of argentic nitrate. It is precipitated in the form of fine, felted needles, even from a dilute solution of the acid; it may be recrystallized from hot water without any essential decomposition, and forms then long, flattened needles. The salt was dried over sulphuric acid for analysis.

- I. 0.9755 grm. substance gave 0.3890 grm. of  $\text{CO}_2$  and 0.0432 grm. of  $\text{H}_2\text{O}$ .  
 II. 0.3200 grm. substance gave, by the method of Carius, 0.3545 grm.  $\text{AgBr}$ .  
 III. 0.7148 grm. substance, precipitated with  $\text{HBr}$ , gave 0.4005 grm.  $\text{AgBr}$ .  
 IV. 0.3668 grm. gave, with  $\text{HBr}$ , 0.2056 grm.  $\text{AgBr}$ .

Calculated for  $\text{AgC}_8\text{HBr}_2\text{O}_2$ .

		I.	II.	Found.	III.	IV.
C	10.69	10.87				
H	0.30	0.49				
Br	47.47		47.14			
Ag	32.05			32.18	32.20	

*Plumbic Dibromacrylate*,  $\text{Pb}(\text{C}_8\text{HBr}_2\text{O}_2)_2$ . The lead salt is precipitated in pearly rhombic scales by the addition of plumbic acetate to a solution of the free acid. It is readily soluble in hot water, sparingly in cold. When dried over sulphuric acid *in vacuo*, it gave:—

- I. 0.3232 grm. substance gave 0.1289 grm.  $\text{CO}_2$  and 0.0230 grm.  $\text{H}_2\text{O}$ .  
 II. 0.4060 grm. gave 0.1858 grm.  $\text{PbSO}_4$ .  
 III. 0.4908 grm. gave 0.2230 grm.  $\text{PbSO}_4$ .

Calculated for $\text{Pb}(\text{C}_3\text{HBr}_2\text{O}_2)_2$ .		Found.		
		I.	II.	III.
C	10.82	10.86		
H	0.30	0.79		
Pb	31.13		31.27	31.05

*Calcic Dibromacrylate*,  $\text{Ca}(\text{C}_3\text{HBr}_2\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ . On neutralizing a solution of the acid with calcic carbonate, and concentrating the solution on the water bath, the calcium salt was obtained in clusters of radiating needles, tolerably soluble even in cold water. The salt gradually effloresced over sulphuric acid, and lost its crystal water completely at  $80-85^\circ$ .

0.7342 grm. of the air-dried salt lost, at  $80-85^\circ$ , 0.0695 grm. of  $\text{H}_2\text{O}$ .

Calculated for $\text{Ca}(\text{C}_3\text{HBr}_2\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ .		Found.
$\text{H}_2\text{O}$	9.78	9.47

0.4951 grm. of the salt, dried at  $80-85^\circ$ , gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1354 grm.  $\text{CaSO}_4$ .

Calculated for $\text{Ca}(\text{C}_3\text{HBr}_2\text{O}_2)_2$ .		Found.
Ca	8.03	8.04

*Potassic Dibromacrylate*,  $\text{KC}_3\text{HBr}_2\text{O}_2$ . The acid neutralized with potassic carbonate and evaporated gave, on cooling, crystals of the potassium salt. From neutral solutions it crystallizes in transparent, six-sided, clustered plates. If but a small amount of free acid is present, it crystallizes in fine, felted needles. Both forms are anhydrous, and do not lose in weight at  $80^\circ$ .

0.5506 grm. gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1792 grm.  $\text{K}_2\text{SO}_4$ .

Calculated for $\text{KC}_3\text{HBr}_2\text{O}_2$ .		Found.
K	14.58	14.61

An acid salt much less soluble in water may be made by adding acid to a solution of the potassium salt. It crystallizes in long needles, which are anhydrous. The salt is not particularly stable, and the excess of acid may be washed out with ether. The salt was dried by exposure to the air, after several recrystallizations from hot water.

- I. 0.6116 grm. substance gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1151 grm.  $\text{K}_2\text{SO}_4$ .  
 II. 0.5395 grm. of substance gave 0.0959 grm.  $\text{K}_2\text{SO}_4$ .

Calculated for  $\text{KC}_5\text{HBr}_2\text{O}_2 \cdot \text{C}_5\text{H}_2\text{Br}_2\text{O}_2$ .

		Found	
		I.	II.
K	7.85	8.45	7.98

*Dibromacrylic Acid.* From the pure barium salt we set free the acid by the addition of hydrochloric acid, and extracted it from the solution with ether. The ether left, upon evaporation, a white, crystalline acid, which was very soluble in alcohol, ether, or chloroform, and but sparingly soluble in benzol, carbonic disulphide, or ligroin. Under water, it melted at about  $20^\circ$ , dissolved in every proportion on heating, and was but slowly volatilized with steam. The acid, when melted under water, could be made to crystallize either by cooling with ice or by the addition of a mineral acid. After recrystallization from benzol, it melted at  $83-84^\circ$ , and this melting point we were unable to raise by further recrystallization from this or other solvents.

Although our analyses left no doubt of the formula of the substance, they showed that it was still impure.

- I. 1.3074 grm. substance gave 0.7692 grm.  $\text{CO}_2$  and 0.1121 grm.  $\text{H}_2\text{O}$ .  
 II. 0.9833 grm. substance gave 0.5797 grm.  $\text{CO}_2$  and 0.0877 grm.  $\text{H}_2\text{O}$ .  
 III. 0.2042 grm. gave 0.3366 grm. AgBr.  
 IV. 0.2447 grm. gave 0.4044 grm. AgBr.  
 V. 0.2083 grm. gave 0.3453 grm. AgBr.  
 VI. 0.2005 grm. gave 0.3309 grm. AgBr.  
 VII. 0.2132 grm. gave 0.3517 grm. AgBr.

Calculated for  $\text{C}_5\text{H}_2\text{Br}_2\text{O}_2$ .

	Calculated for $\text{C}_5\text{H}_2\text{Br}_2\text{O}_2$			Found.			
	I.	II.	III.	IV.	V.	VI.	VII.
C	15.65	16.04	16.08				
H	0.87	0.95	0.99				
Br	69.56		70.15	70.33	70.53	70.23	70.20

Our results had sufficiently established the fact that a dibromacrylic acid was formed from mucobromic acid by the action of baric hydrate in the cold, but a more extended investigation of it was evidently needed to determine the nature of the impurity which was so difficult of removal. Since Wallach and Reincke\* had shortly before an-

\* Berichte der deutsch. chem. Gesellsch. x. 2128.

nounced that they were engaged in making from bromalid a dibrom-acrylic acid, which we thought probable, although upon very insufficient grounds, would prove to be identical with ours, we felt compelled for the moment to suspend our investigations. The other portions of the re-search afterward claimed so much attention that no study of the acid has yet been made sufficiently extended to establish the conditions essential to its preparation in a pure state. It has been found, however, that an acid melting at 84–85° contains but a slight excess of bromine (I.), and that the pure acid (II.) melts at 85–86°.

- I. 0.2204 grm. substance gave 0.3621 grm. AgBr.  
 II. 0.2650 grm. substance gave 0.4336 grm. AgBr.

Calculated for  $C_3H_2Br_2O_3$ .

Found.

		I.	II.
Br	69.56	69.90	69.65

For purposes of comparison, certain determinations of the solubility of the acid and its barium salt may find a place here, although they were not made with absolutely pure material, and are therefore subject to revision. In determining the solubility of the acid, the saturated solution, made according to the method of V. Meyer, was neutralized with baric carbonate, and the dissolved barium determined by precipitation with sulphuric acid.

- I. 14.7798 grm. of a solution, saturated at 20°, gave 0.4488 grm.  $BaSO_4$ .  
 II. 8.6788 grm. of a solution, saturated at 20°, gave 0.2630 grm.  $BaSO_4$ .

According to these determinations, an aqueous solution of the acid, saturated at 20°, contains the percentages:—

I.	II.
5.98	5.98

8.4992 grm. of a solution of the barium salt, saturated at 20°, gave, on evaporation with  $H_2SO_4$  and ignition, 0.1912 grm.  $BaSO_4$ .

The aqueous solution of baric dibromacrylate, saturated at 20°, therefore contains 5.74 per cent of the dry salt.

In studying the behavior of this dibromacrylic acid towards reagents, we have been able to use only the product melting at 83–84°, which may easily be obtained in any quantity desired. When boiled with an excess of baric hydrate, the acid is completely decomposed, baric carbonate is precipitated, bromacetylen set free, and at the same time baric malonate is formed in abundance. For complete identification,



the baric malonate was converted into the lead salt, and the latter analyzed.

0.5179 grm. of the salt, dried at  $110^{\circ}$ , gave, on ignition with  $\text{H}_2\text{SO}_4$ ,  
0.5062 grm.  $\text{PbSO}_4$ .

Calculated for  $\text{PbC}_3\text{H}_4\text{O}_4$ .  
66.99

Found.  
66.79

The amount of baric malonate formed in this decomposition with an excess of baric hydrate was found to be forty-nine per cent of the theoretical yield as the mean of two determinations.

The behavior of the acid towards hydrobromic acid was studied by Mr. C. F. Mabery. It is not altered by ordinary concentrated hydrobromic acid (b. pt.  $126^{\circ}$ ), nor is it affected in the cold by an acid saturated at  $0^{\circ}$ ; but it forms an addition-product when heated with it for several hours at  $100^{\circ}$ . The reaction is by no means neat, and a large portion of the substance is charred. The tribromopropionic acid which is thus formed differs essentially in its melting-point ( $116$ – $117^{\circ}$ ) and other physical properties from the acid melting at  $93^{\circ}$  mentioned by Linnemann and Penl,\* and recently more fully described by Michael and Norton;† and also from the acid melting at  $53^{\circ}$ , which was obtained by Fittig and Petri,‡ by the action of hydrobromic acid upon their dibromacrylic acid. It is sparingly soluble in cold water, readily in hot, and may be crystallized without difficulty from hot water. It is readily soluble in alcohol or ether, somewhat less soluble in chloroform. From water it crystallizes in pearly scales, which melt at  $116$ – $117^{\circ}$ . Argentic nitrate precipitates from an aqueous solution of the acid, the silver salt in clustered rhombic plates.

0.1892 grm. of the acid gave 0.3453 grm.  $\text{AgBr}$ .

Calculated for  $\text{C}_3\text{H}_4\text{Br}_3\text{O}_2$ .  
Br 77.16

Found.  
77.64

If one molecule of bromine is added to dibromacrylic acid dissolved in chloroform, the color of the bromine gradually disappears, and after the lapse of some time tetrabromopropionic acid separates in large, well-formed crystals, which melt at  $125^{\circ}$ . This acid is at present under investigation in this laboratory.

\* Berichte der deutsch. chem. Gesellsch., viii. 1098.

† Amer. Chem. Journ., ii. 18.

‡ Ann. Chem. u. Pharm., cxcv. 73.

One well-marked product of the decomposition of mucobromic acid by cold baric hydrate had been shown to be baric dibromacrylate; it only remained to study the more soluble products of the reaction. In continuing the investigation with Mr. O. R. Jackson, the filtrate from the crystals of baric dibromacrylate was treated with carbonic dioxide to remove the excess of baric hydrate, filtered from the baric carbonate, and the filtrate evaporated at a gentle heat ( $40-50^{\circ}$ ). In the course of this evaporation, a certain amount of baric dibromacrylate crystallized out, which was removed from time to time. When the liquid had been reduced to about one third its original volume, it was precipitated by the addition of two volumes of alcohol. The bulky crystalline precipitate thus thrown down proved upon qualitative examination to consist chiefly of baric formiate. When purified by repeated precipitation from aqueous solution by alcohol and recrystallization from water, it showed the characteristic form of baric formiate.

0.3964 gm. substance gave, on ignition with  $H_2SO_4$ , 0.4054 gm.  $BaSO_4$ .

	Calculated for $Ba(CHO_2)_2$ .	Found.
Ba	60.36	60.13

The lead salt made from the barium salt crystallized in the characteristic form of plumbic formiate, and gave on analysis the required percentage of lead.

0.4149 gm. of the salt gave, on ignition with  $H_2SO_4$ , 0.4221 gm.  $PbSO_4$ .

	Calculated for $Pb(CHO_2)_2$ .	Found.
Pb	69.69	69.50

In the alcoholic filtrate from the baric formiate, we were able to find, beside baric bromide, only a crystallizable barium salt, well marked by its qualitative reactions, but so unstable that we were not able to effect its purification. The behavior of this salt, and the analyses which we made of it in an impure state, led us to the conclusion that it was the barium salt of brompropionic acid, formed by subtraction of hydrobromic acid from the dibromacrylic; and this view was subsequently proved to be correct by a study of the addition products which the corresponding acid formed with the halogens and the haloid acids.

Since all our attempts to isolate a pure salt from a solution containing baric bromide had proved unsuccessful, we attempted to take advantage of a remarkably stable molecular compound which the corresponding acid forms with dibromacrylic acid. This compound

may readily be made by acidifying the baric hydrate solution of mucobromic acid, without removing the separated baric dibromacrylate, and extracting the solution with ether. The same compound, although in smaller quantity, may also be obtained, after that portion of the barium salt which separates spontaneously is removed. From dibromacrylic acid it may be made by the action of baric hydrate in the cold. For its preparation we usually have employed a solution of potassic, instead of baric, hydrate. The proportions which we have found most advantageous are 70 grm. of potassic hydrate and 400 c.c. of water to 100 grm. of mucobromic acid. Care must be taken in adding the mucobromic acid, and also in the subsequent acidification with hydrochloric acid, that no sensible elevation of temperature takes place. When the solution is partially acidified, the acid potassium salt of dibromacrylic acid usually separates in abundance, but dissolves upon further addition of acid. The solution is then thoroughly extracted with ether; and this leaves on distillation a liquid residue, which, on cooling, gradually solidifies in large, well-formed, monoclinic (?) prisms. These are readily soluble in water, alcohol, ether, or chloroform, and may be purified by crystallization from hot benzol, or more conveniently by melting with a little water. Thus purified, the substance melts at  $104-105^{\circ}$ ; and this melting point is not altered by repeated recrystallizations from various solvents.

- I. 0.9023 grm. substance gave 0.6440 grm.  $\text{CO}_2$  and 0.0850 grm.  $\text{H}_2\text{O}$ .
- II. 0.4403 grm. substance gave 0.3157 grm.  $\text{CO}_2$  and 0.0433 grm.  $\text{H}_2\text{O}$ .
- III. 0.2263 grm. substance gave 0.3386 grm. AgBr.
- IV. 0.2241 grm. substance gave 0.3321 grm. AgBr.
- V. 0.2092 grm. substance gave 0.3139 grm. AgBr.

Calculated for $\text{C}_6\text{H}_5\text{Br}_2\text{O}_4$ .		Found.				
		I.	II.	III.	IV	V.
C	19.00	19.43	19.54			
H	0.79	1.05	1.09			
Br	63.33			63.66	63.03	63.84

Although the percentages we have found show a considerable variation from those calculated for equal molecules of dibromacrylic and brompropionic acids, they agree better with this than with any other formula equally simple; and, moreover, the qualitative behavior of the substance is such as to render this formula tolerably certain. Its

aqueous solution gives, on the addition of plumbic acetate, an immediate crystalline precipitate of plumbic dibromacrylate.

0.3560 grm. gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1628 grm.  $\text{PbSO}_4$ .

	Calculated for $\text{Pb}(\text{C}_9\text{HBr}_2\text{O}_2)_2$	Found.
Pb	31.13	31.25

So also if it is neutralized with baric carbonate, the solution gives, on spontaneous evaporation, crystals of baric dibromacrylate, while in solution remains a much more soluble salt, with all the characters of baric brompropiolate. That this substance contains the brompropionic acid is shown by the evolution of carbonic dioxide and bromacetylen when its aqueous evolution is boiled.

Starting with this molecular compound melting at  $104-105^\circ$ , we made various attempts to isolate the brompropionic acid and its salts in a pure state. The barium salts of dibromacrylic and brompropionic acids showed such marked differences in their solubility in water or in alcohol that we hoped through them to effect a complete separation of the two acids. We found, however, that it was difficult to obtain in this way a colorless salt of brompropionic acid which appeared even tolerably pure. We therefore attempted to separate the two acids by converting them into their ethyl-ethers and submitting these to fractional distillation. We dissolved the molecular compound (m. pt.  $104^\circ$ ) in absolute alcohol, added concentrated sulphuric acid, and warmed. The ethers soon separated in part, and were precipitated with water, washed with dilute sodic carbonate, and dried over fused calcic chloride. These mixed ethers had an extremely sharp, pungent odor, and their vapor attacked the eyes violently. On attempting to separate the two by distillation, we found that a large portion of the liquid was carbonized in each distillation, and that but one volatile product could be isolated. This was a mobile liquid, of an agreeable aromatic odor, which boiled between  $209$  and  $215^\circ$ , without any very noticeable decomposition. The portion of this which boiled between  $212-214^\circ$  was analyzed, and found to be essentially the ethyl-ether of dibromacrylic acid, although still impure. Since our chief object was to isolate the ether of the brompropionic acid, and this had evidently been for the most part destroyed, the substance was not farther examined.

0.5235 grm. of substance gave, on combustion, 0.4675 grm.  $\text{CO}_2$  and 0.1250 grm.  $\text{H}_2\text{O}$ .

	Calculated for $C_4HBr_2O_2 \cdot C_2H_4$	Found.
C	23.23	24.36
H	2.33	2.65

Finally, we attempted to separate the two acids by fractional saturation. Although the products thus obtained gave us analytical results that were far from satisfactory, we found that the separation could be effected with tolerable precision, the brompropionic acid being the stronger acid, and that this was the most convenient way of preparing material sufficiently pure for further work, in any considerable quantity. Pure substance melting at  $104-105^\circ$  was dissolved in water, and a little less than the calculated amount of baric carbonate was added. The clear solution was then freed as completely as possible from dibromacrylic acid by repeated extraction with ether, and the baric brompropionate obtained by spontaneous evaporation.

Our analytical results show that the material analyzed was not pure, and yet they leave no doubt as to its nature.

- I. 0.6974 grm. of substance, dried over  $H_2SO_4$ , gave 0.3968 grm.  $CO_2$  and 0.0347 grm.  $H_2O$ .
- II. 0.3060 grm. of substance, dried over  $H_2SO_4$ , gave 0.1657 grm.  $BaSO_4$ .
- III. 0.1829 grm. of substance, dried over  $H_2SO_4$ , gave 0.0973 grm.  $BaSO_4$ .
- IV. 0.4325 grm. of substance, dried over  $H_2SO_4$ , gave 0.2305 grm.  $BaSO_4$ .

	Calculated for $Ba(C_3BrO_2)_2$	Found.			
		I.	II.	III.	IV.
C	16.63	15.52			
H	—	0.55			
Ba	31.63		31.84	31.27	31.32

We have been unable to make any satisfactory determinations of the water of crystallization, since the salt cannot be heated, and even on standing over sulphuric acid in the cold it is slowly decomposed. The salt when crystallized from water probably contains four molecules of water.

- I. 2.1104 grm. of the air-dried salt lost over sulphuric acid 0.2803 grm.
- II. 0.9828 grm. of air-dried substance lost over  $H_2SO_4$  0.1316 grm.

	Calculated for $Ba(C_3BrO_2)_2 \cdot 4H_2O$	Found.	
		I.	II.
$H_2O$	14.26	13.28	13.39

In one instance the salt precipitated from alcoholic solution by the addition of ether was found to contain but a single molecule of water.

1.0639 grm. of air-dried salt lost over  $\text{H}_2\text{SO}_4$  *in vacuo* 0.0458 grm.

	Calculated for $\text{Ba}(\text{C}_3\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	3.99	4.30

The salt usually crystallized, on the slow evaporation of its aqueous solution, in small, oblique prisms; but it sometimes separated, on long standing, in more compact, clustered, rhombic plates. When dry, it is decomposed quite rapidly at  $50^\circ$ , and deflagrates at about  $125^\circ$ . In aqueous solution it is recomposed on boiling, with the precipitation of baric carbonate and the evolution of carbonic dioxide and bromacetylen. From solutions containing an excess of the acid, a somewhat more stable salt separates in fine, felted needles, less soluble in water than the neutral salt. This would seem to be an acid salt, corresponding to the acid potassium salt of dibromacrylic acid; but we could obtain no satisfactory analytical results.

When argentic nitrate is added to a solution of the barium salt, or of the free acid, a white, amorphous silver salt is precipitated, and at the same time if the solution is concentrated the evolution of carbonic dioxide is noticed. The precipitate turns yellow on washing, and is evidently still further decomposed on drying. When gently warmed with water, it is slowly decomposed; but, when suddenly heated nearly to  $100^\circ$ , it explodes violently, with the separation of large quantities of carbon. In a dry state it explodes when heated to about  $75^\circ$ . In dilute nitric acid it dissolves at first; but the solution soon grows turbid, smells strongly of bromacetylen, and argentic bromide is precipitated. One could hardly expect trustworthy results from the analysis of so unstable a substance. One silver determination, however, showed that it must be considered a derivative of bromacetylen, rather than of brompropionic acid.

0.2313 grm. of substance, dried over  $\text{H}_2\text{SO}_4$  *in vacuo*, gave 0.1975 grm. AgBr.

	Calculated for $\text{AgC}_3\text{BrO}_3$ ; for $\text{AgC}_2\text{Br}$ .	Found.
Ag	42.19      50.94	49.05

Although the barium salt had given unsatisfactory results on analysis, we made from it the acid, and hoped then to be able to effect its purification. We therefore precipitated the barium from a cold, aqueous solution, with a slight excess of sulphuric acid, and extracted the acid from the filtered solution with ether. We obtained in this

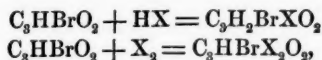
way long, slender prisms, extremely soluble in water, alcohol, or ether, readily in chloroform or benzol, more sparingly in carbonic disulphide, and but slightly soluble in ligroin. The crystals obtained from aqueous solution by spontaneous evaporation appeared to contain water of crystallization. When pressed with paper they melted at 60–65°; but over sulphuric acid they soon became opaque, and the melting point had risen to 80° or over.

We attempted the purification of the acid by repeated recrystallization from ligroin to which a little ether had been added. The long, silky needles thus obtained melted at 86°, but gave on analysis no satisfactory results (I. and II.). Although the acid was blackened and apparently completely decomposed at a temperature but little over 100°, we found that it could be sublimed readily between watch-glasses at steam heat. The melting point was, however, lowered rather than raised, by successive sublimations, and analyses (III. and IV.) of the sublimed product gave too high a percentage of bromine.

- I. 0.3010 grm. substance gave 0.4025 grm. AgBr.
- II. 0.1198 grm. substance gave 0.1582 grm. AgBr.
- III. 0.2010 grm. substance gave 0.2580 grm. AgBr.
- IV. 0.1820 grm. substance gave 0.2339 grm. AgBr.

Calculated for $C_3HBrO_2$ .		Found.			
		I.	II.	III.	IV.
Br	53.69	56.90	56.21	54.63	54.69

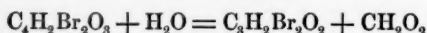
The acid is decomposed, with the formation of carbonic dioxide and bromacetylen, on boiling its aqueous solution. When heated with an excess of baric hydrate, baric carbonate is precipitated, bromacetylen is evolved, and at the same time baric malonate is formed in abundance. It unites with dibromacrylic acid immediately to form the characteristic addition-product. An ethereal solution containing a mixture of the two acids, approximately in molecular proportions, gave on evaporation a substance which, without purification, melted at 103°. With the halogens and haloid acids, it forms addition-products with the greatest readiness. The substituted acrylic acids which are thus formed, according to the equations, —



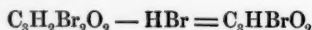
are easily purified, and their formation can leave no doubt of the nature of the brompropionic acid. Several of these acids will be described later in this paper.



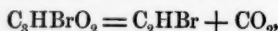
The decomposition of mucobromic acid by baric hydrate, under the conditions described, may be expressed by the following equations. The first action would seem to be the assimilation of a molecule of water and the formation of dibromacrylic and formic acids.



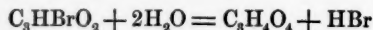
This action is immediately followed, even in the cold, by the subtraction of hydrobromic acid, —



The brompropionic acid is then either decomposed by heat, —



or is converted into malonic acid, —



Since a large percentage of dibromacrylic acid was converted into brompropionic acid in this reaction, and it had previously been proved that a portion of the mucobromic acid entirely escaped decomposition when the proportion of baric hydrate was materially lessened, I recently attempted to increase the yield by reversing the mode of procedure. I therefore added baric hydrate, gradually, to mucobromic acid suspended in a little water; taking care, after the acid was neutralized, to make the solution but slightly alkaline, and to wait until it was again neutral before further addition. I found, however, that an entirely different reaction had taken place under these conditions, and that among the products of this reaction little or no dibromacrylic acid could be found. This decomposition is at present under investigation in this laboratory, and all discussion of the results we have already obtained must therefore be reserved for a subsequent paper.

#### MUCOCHLORIC ACID.

Mucochloric acid was discovered in 1865 by Schmelz and Beilstein,\* and since that time, as far as I know, it has never been further studied. The discoverers found its preparation so very laborious, and the yield which they obtained so small, that they made no extended investigation of it, but contented themselves with giving a short description of the acid, together with the analyses necessary to establish its composition. Although their account was certainly not encourag-

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\* Ann. Chem. u. Pharm., Suppl., iii. 280.



ing, it seemed to me worth while to attempt its preparation, more especially in order to study the dichloracrylic acid derived from it, and to compare this with the acid of the same composition which Wallach\* had already made from chloralid. This investigation Mr. W. Z. Bennett undertook with me.

The method followed by Schmelz and Beilstein in making mucochloric acid was as follows: Pyromucic acid suspended in water was treated with chlorine at first in the cold and afterwards at boiling heat. When all action appeared to be over, the solution was somewhat concentrated on the water bath, and finally brought to crystallization by evaporation over sulphuric acid *in vacuo*. This method gave in our hands precisely the same discouraging quantitative results that Schmelz and Beilstein had obtained; and it was only after a long series of unsuccessful experiments that we succeeded in finding a simple modification of the method which enabled us to prepare material sufficient for investigation. We suspended the pyromucic acid in ten times its weight of water, cooled the whole well with ice, and passed in a rapid stream of chlorine until the liquid was thoroughly saturated. The temperature was carefully kept within a few degrees of the freezing point during this treatment with chlorine, and not unfrequently considerable quantities of the crystalline hydrate of chlorine separated. When the solution was saturated it was heated to boiling, after a few moments again cooled to 0°, and saturated once more with chlorine. When this operation had been repeated several times, crystals of mucochloric acid began to appear as the solution cooled. At first we filtered these crystals off, and subjected the filtrate to further treatment; but we found by experience that little or no product was gained after the sixth chlorination, and we, therefore, usually proceeded to this point before we removed the acid formed. We then collected the crystals which separated as the solution cooled, and evaporated the mother liquors on the water bath to the point of crystallization. The crystals were drained, pressed, and recrystallized from hot water. We further found it convenient to add to the pyromucic acid a small percentage of iodine. Although this was by no means essential, we found that our results were then more constant and the average yield greater. As the result of several preparations which we made in the course of the investigation, we obtained 129 grm. of mucochloric acid from 202 grm. of pyromucic acid. This corresponds to a little more than forty per

\* Berichte der deutsch. chem. Gesellsch., viii. 1580.

cent of the theoretical amount, as our average product, although in single instances our yield has reached 50 per cent. The product made in this way crystallized from water in well-formed rhombic plates, which in their properties agreed in every particular with the description of Schmelz and Beilstein. The acid melted at  $125^{\circ}$ , and was very soluble in alcohol or ether, sparingly soluble in cold water, readily in hot. Boiling benzol or chloroform dissolved it with readiness, while in carbonic disulphide or ligroin it was almost insoluble. The purity of our material was shown by the following analyses:—

- I. 0.7408 grm. substance gave 0.7617 grm.  $\text{CO}_2$  and 0.0831 grm.  $\text{H}_2\text{O}$ .  
 II. 0.5512 grm. substance gave 0.5687 grm.  $\text{CO}_2$  and 0.0621 grm.  $\text{H}_2\text{O}$ .  
 III. 0.2090 grm. substance gave 0.3564 grm.  $\text{AgCl}$ .

Calculated for $\text{C}_6\text{H}_2\text{Cl}_4\text{O}_3$ .		Found.		
		I.	II.	III.
C	28.40	28.06	28.13	
H	1.18	1.25	1.25	
Cl	42.01			42.16

Although mucochloric acid appears to form derivatives in some respects more stable and readily studied than the corresponding derivatives of mucobromic acid, we have thus far taken up more in detail only the dichloracrylic acid which may easily be made from it by the action of alkalis.

#### *Dichloracrylic Acid.*

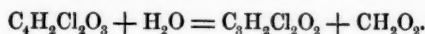
In 1877, Wallach\* obtained a dichloracrylic acid as a product of the reduction of chloralid. This acid was afterward more carefully studied by Wallach and Hunäus,† and quite recently Wallach‡ has published a paper still further describing the acid and its salts, and correcting the work of Hunäus in several important particulars. At the time this investigation was begun, this acid was the only disubstituted acrylic acid known, and since its constitution was fairly established by the mode of its preparation, it seemed desirable to prepare the dichloracrylic acid from mucochloric, in order to compare the two acids.

\* Berichte der deutsch. chem. Gesellsch., viii. 1580.

† Berichte der deutsch. chem. Gesellsch., x. 567. Ann. Chem. u. Pharm. cxliii. 19.

‡ Ann. Chem. u. Pharm. cciii. 83.

The decomposition of mucochloric acid into dichloracrylic and formic acids, under the influence of alkalis, is much more neatly accomplished than the corresponding reaction with mucobromic acid. Under ordinary conditions, but little hydrochloric acid is split off, and the yield of dichloracrylic acid is nearly 90 per cent of that required by the equation,—



We never have noticed in the preparation of dichloracrylic acid either chlorpropionic acid or any compound corresponding to that which brompropionic acid forms with dibromacrylic. We usually have dissolved mucochloric acid in quite an excess of potassic hydrate, allowed the solution to stand for a short time, acidified with hydrochloric acid, and extracted with ether. The dichloracrylic acid left on evaporation of the ether may be purified by melting it several times with a little water. When dried over sulphuric acid it gave the following results on analysis:—

- I. 0.5280 grm. substance gave 0.4894 grm.  $\text{CO}_2$  and 0.0720 grm.  $\text{H}_2\text{O}$ .  
 II. 0.3670 grm. substance gave 0.3399 grm.  $\text{CO}_2$  and 0.0477 grm.  $\text{H}_2\text{O}$ .  
 III. 0.1037 grm. substance gave 0.2123 grm.  $\text{AgCl}$ .  
 IV. 0.2674 grm. substance gave 0.5420 grm.  $\text{AgCl}$ .

Calculated for $\text{C}_3\text{H}_2\text{Cl}_2\text{O}_2$ .		Found.			
		I.	II.	III.	IV.
C	25.54	25.28	25.25		
H	1.42	1.51	1.45		
Cl	50.36			50.62	50.10

This dichloracrylic acid forms small rhombic prisms which volatilize rapidly on exposure to the air. It is readily soluble in water, alcohol, ether, or chloroform, and it also dissolves freely in boiling benzol, carbonic disulphide, or ligroin. It melts at  $85-86^\circ$ , and, when solidified by quick cooling, melts again at the same temperature. The  $\beta$  dichloracrylic acid of Wallach, on the other hand, melts at  $76-77^\circ$  and its melting point falls to  $63-64^\circ$  when melted and suddenly cooled.

*Argentio Dichloracrylate*,  $\text{AgC}_3\text{HCl}_2\text{O}_2$ . The silver salt was precipitated in the form of fine felted needles on the addition of argentic nitrate even to a dilute solution of the acid. The salt was quite stable and could be recrystallized from hot water without any marked decomposition.

- I. 0.5460 grm. substance gave 0.2808 grm.  $\text{CO}_2$  and 0.0299 grm.  $\text{H}_2\text{O}$ .  
 II. 0.4819 grm. substance gave 0.2494 grm.  $\text{CO}_2$  and 0.0253 grm.  $\text{H}_2\text{O}$ .  
 III. 0.2511 grm. substance gave, by Cairus' method, 0.2910 grm.  $\text{AgCl}$ .  
 IV. 0.2078 grm. substance gave, by Cairus' method, 0.2401 grm.  $\text{AgCl}$ .  
 V. 0.2089 grm. substance, precipitated by  $\text{HCl}$ , gave 0.1209 grm.  $\text{AgCl}$ .  
 VI. 0.6768 grm. substance, precipitated by  $\text{HCl}$ , gave 0.3909 grm.  $\text{AgCl}$ .

Calculated for $\text{AgC}_3\text{HCl}_2\text{O}_2$ .				Found.			
		I.	II.	III.	IV.	V.	VI.
C	14.52	14.03	14.12				
H	0.40	0.60	0.58				
Cl	28.63			28.65	28.56		
Ag	43.54					43.55	43.49

*Baric Dichloracrylate*,  $\text{Ba}(\text{C}_3\text{HCl}_2\text{O}_2)_2 \cdot \text{H}_2\text{O}$ . The barium salt was prepared by neutralizing the aqueous solution of the acid with baric carbonate and concentrating the solution upon the water bath. On cooling, the salt separated in rhombic plates which were permanent in the air, and did not lose in weight over sulphuric acid *in vacuo*.

- I. 0.2185 grm. of the salt lost, when heated to  $80^\circ$ , 0.0088 grm.  $\text{H}_2\text{O}$  and gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1174 grm.  $\text{BaSO}_4$ .  
 II. 0.1941 grm. of the salt gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1041 grm.  $\text{BaSO}_4$ .  
 III. 0.2402 grm. of the salt gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1281 grm.  $\text{BaSO}_4$ .  
 IV. 0.9167 of the salt lost, when heated to  $80^\circ$ , 0.0395 grm.  $\text{H}_2\text{O}$ .

Calculated for $\text{Ba}(\text{C}_3\text{HCl}_2\text{O}_2)_2 \cdot \text{H}_2\text{O}$ .				Found.			
		I.	II.	III.	IV.		
Ba	31.49	31.59	31.53	31.36			
$\text{H}_2\text{O}$	4.14	4.03			4.31		

For the further characterization of this salt we determined its solubility in cold water by the method of V. Meyer.

- I. 5.6625 grm. of an aqueous solution, saturated at  $18^\circ$ , gave, on evaporation and ignition with  $\text{H}_2\text{SO}_4$ , 0.1956 grm.  $\text{BaSO}_4$ .  
 II. 2.416 grm. of a solution, saturated at  $18^\circ.5$ , gave 0.0801 grm.  $\text{BaSO}_4$ .

These determinations give as the percentages of the anhydrous salt contained in the hot solutions saturated at 18° and 18°.5 respectively

I.	II.
6.28	6.19

*Calcic Dichloracrylate*,  $\text{Ca}(\text{C}_3\text{HCl}_2\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ . The calcium salt, which was extremely soluble in water, was made by neutralizing a solution of the acid with calcic carbonate. On cooling the concentrated solution, the salt separated in long, flat radiating needles, which were permanent in the air, but slowly effloresced over sulphuric acid.

- I. 0.4077 grm. of the air-dried salt lost, on heating to 95–100°, 0.0580 grm.  $\text{H}_2\text{O}$ , and gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1488 grm.  $\text{CaSO}_4$ .
- II. 0.6163 grm. of the air-dried salt lost, on heating, 0.0875 grm.  $\text{H}_2\text{O}$ .
- III. 0.3217 grm. of the dried salt (II.), corresponding to 0.3749 grm. of the air-dried salt, gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1348 grm.  $\text{CaSO}_4$ .

Calculated for  $\text{Ca}(\text{C}_3\text{HCl}_2\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ .

		I.	Found.	II.	III.
Ca	10.69	10.73			10.58
$\text{H}_2\text{O}$	14.43	14.23	14.20		

*Potassic Dichloracrylate*,  $\text{KC}_3\text{HCl}_2\text{O}_2$ . The potassium salt crystallizes from a solution of mucochloric acid in an excess of potassic hydrate (1 : 4) when this is strongly cooled. Although it is quite soluble even in cold water, it may readily be purified by recrystallization from hot water. From concentrated solutions it crystallizes on cooling in long, slender needles, which are anhydrous.

- I. 0.3054 grm. of the salt gave, on ignition and evaporation with  $\text{HCl}$ , 0.1283 grm.  $\text{KCl}$ .
- II. 0.2159 grm. of the salt gave 0.0908 grm.  $\text{KCl}$ .

Calculated for  $\text{KC}_3\text{HCl}_2\text{O}_2$ .

		I.	Found.	II.
K	21.84	22.03		22.06

The foregoing results seemed to us to show with sufficient precision that our acid was essentially different from the  $\beta$  dichloracrylic acid of Wallach, since the two acids differed markedly in their physical properties, and their salts were also quite dissimilar. Following the

analyses of Hunäus, Wallach\* had assigned to the barium salt of the  $\beta$  dichloracrylic acid the formula  $\text{Ba}(\text{C}_3\text{HCl}_2\text{O}_2)_2 \cdot 5\text{H}_2\text{O}$ , and to the calcium salt the probable formula  $\text{Ca}(\text{C}_3\text{HCl}_2\text{O}_2)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ ; while the corresponding salts of our acid we had found to have the formulæ  $\text{Ba}(\text{C}_3\text{HCl}_2\text{O}_2)_2 \cdot \text{H}_2\text{O}$  and  $\text{Ca}(\text{C}_3\text{HCl}_2\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ . Although the potassium salt of neither acid contained water of crystallization, one crystallized in plates, the other in needles.

Quite recently Wallach† has published the results of several determinations made since the publication of a preliminary notice‡ of our dichloracrylic acid. These determinations show that the formulæ which had previously been assigned to the barium and calcium salts of his acid were incorrect, and that they probably each contained two molecules of water. To these determinations, however, Wallach would attach but little weight for the identification of the acid, although he considers the isomerism of the two dichloracrylic acids to be fully established.

“Ich möchte aber nach den gemachten Erfahrungen diesen Bestimmungen vorläufig keinen besonderen Werth für die *Charakterisirung* der Dichloracrylsäure aus Chloralid beilegen. Man wird besser thun, sich dafür an die scharf bestimmbaren Eigenschaften der *gemessenen freien Säure* und allenfalls an die tafelförmige Ausbildung des wasserfreien Kalisalzes, sowie an die angegebenen krystallographischen Daten des Baryumsalzes, anstatt an die bisher ausgeführten Wasserbestimmungen zu halten; für letztere müssen noch weitere Versuche vorbehalten bleiben. Jedenfalls muss aber der Zweck der obigen Angaben jetzt schon als erreicht bezeichnet werden: nämlich die völlige *Verschiedenheit der Dichloracrylsäure aus Chloralid* der nur die Formel  $\text{CCl}_2 = \text{CH} - \text{CO}_2\text{H}$  zukommen kann, *von der, welche Bennett und Hill aus Mucochlorsäure erhielten definitiv zu bestätigen.*” §

Unfortunately we have as yet been unable to obtain either our acid or its barium salt in a form which would admit of crystallographic study. Still, the differences already established leave no reasonable doubt that the two acids are isomeric, and the acid from mucochloric acid may therefore be distinguished for convenience as the  $\alpha$  dichloracrylic acid.

The behavior of this acid towards reagents has thus far been little

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\* Ann. Chem. u. Pharm., cxcii. 23.

† Ibid., cciii. 83.

‡ Berichte der deutsch. chem. Gesellsch., xii. 655.

§ Loc. cit., p. 86.

examined. On boiling with an excess of baric hydrate, it is decomposed in essentially the same way as the dibromacrylic acid, baric malonate being formed in abundance. This decomposition with alkalis we have not followed further, since it was evident that chlorpropionic acid should be the intermediate product formed; and we wished not to interfere with the researches which Wallach had already undertaken with Bischof,\* concerning the decomposition of  $\beta$  dichloracrylic acid by alkalies.

Although the acid does not add bromine when heated with it to  $100^\circ$  in chloroform solution, it readily forms an addition product when heated for some time with undiluted bromine at  $100^\circ$ . The dichloridibrompropionic acid which is thus formed is at present under investigation in this laboratory.

#### SUBSTITUTED ACRYLIC ACIDS FROM BROMPROPIOLIC ACID.

Mr. C. F. Mabery has studied with me some of the substituted acrylic acids which may readily be made by the addition of halogens or haloid acids to brompropionic acid.

##### *Dibromacrylic Acid of Fittig and Petri.*

Brompropionic acid dissolves easily in concentrated hydrobromic acid (b. pt.  $126^\circ$ ), and on standing for a short time the solution deposits abundant crystals of a dibromacrylic acid, which is identical with that described by Fittig and Petri as resulting from the decomposition of tribromsuccinic acid. This acid may also be prepared to advantage from the solution of baric brompropionate and baric bromide which is obtained in the preparation of baric dibromacrylate by the action of baric hydrate upon mucobromic acid. It is only necessary to precipitate the barium with dilute sulphuric acid, and to concentrate the solution upon the water bath. The acid which separates as the solution cools is easily purified by recrystallization.

From a hot concentrated solution, the acid falls at first as an oil; but, after the solution has cooled somewhat, it separates in pearly scales, which melt at  $85-86^\circ$ . In analysis they gave the required percentage of bromine.

0.2614 grm. of substance gave 0.4283 grm. AgBr.

Calculated for $C_3H_2Br_2O_2$ .		Found.
Br	69.57	69.72

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\* Berichte der deutsch. chem. Gesellsch., xi. 751; xii. 57.



The solubility of the acid in water at ordinary temperatures we determined by neutralizing with baric carbonate the solution made according to V. Meyer's method, and evaporating the filtered solution with sulphuric acid.

- I. 12.5364 grm. of a solution, saturated at 20°, gave 0.2070 grm.  $\text{BaSO}_4$ .
- II. 11.6241 grm. of a solution, saturated at 20°, gave 0.1712 grm.  $\text{BaSO}_4$ .
- III. 8.4358 grm. of a solution, saturated at 20°, gave 0.1248 grm.  $\text{BaSO}_4$ .
- IV. 10.6740 grm. of a solution, saturated at 20°, gave 0.1581 grm.  $\text{BaSO}_4$ .

As the result of these determinations, we find that an aqueous solution of the acid saturated at 20° contains the following percentages:—

I.	II.	III.	IV.
3.16	2.91	2.92	2.93

Fittig and Petri found that the dibromacrylic acid made from tri-bromsuccinic gave at 20° a solution which contained 3.355 per cent of the acid.

*Baric Dibromacrylate*,  $\text{Ba}(\text{C}_3\text{HBr}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ . An aqueous solution of the acid was neutralized with baric carbonate, and the filtered solution evaporated on the water bath. On cooling, the barium salt crystallized in rectangular plates, whose angles were, however, often more or less modified.

The air-dried salt lost, on heating to 100°, two molecules of water.

- I. 0.4018 grm. of air-dried salt lost at 100° 0.0226 grm.  $\text{H}_2\text{O}$ .
- II. 0.4644 grm. of air-dried salt lost at 100° 0.0261 grm.  $\text{H}_2\text{O}$ .
- III. 0.5086 grm. of air-dried salt lost at 100° 0.0299 grm.  $\text{H}_2\text{O}$ .

Calculated for  $\text{Ba}(\text{C}_3\text{HBr}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ .

		I.	II.	III.
$\text{H}_2\text{O}$	5.71	5.62	5.62	5.88

The anhydrous salt then gave:—

- I. 0.3425 grm. of substance, dried at 100°, gave on ignition 0.1353 grm.  $\text{BaSO}_4$ .
- II. 0.4383 grm. of the salt, dried at 100°, gave 0.1723 grm.  $\text{BaSO}_4$ .
- III. 0.2934 grm. of the salt, dried at 100°, gave 0.1153 grm.  $\text{BaSO}_4$ .

Calculated for  $\text{Ba}(\text{C}_3\text{HBr}_2\text{O}_2)_2$ .

		I.	II.	III.
Ba	23.03	23.23	23.11	23.10



Fittig and Petri found in two determinations of water, in the barium salt of their acid, a somewhat higher percentage (6.73 and 7.27), and therefore assign it the formula  $\text{Ba}(\text{C}_3\text{HBr}_2\text{O}_2)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  — (calculated 7.03 per cent).

The solubility of the salt we determined by V. Meyer's method.

- I. 3.9749 grm. of a solution, saturated at  $23^\circ$ , gave, on evaporation with  $\text{H}_2\text{SO}_4$  and ignition, 0.1748 grm.  $\text{BaSO}_4$ .
- II. 3.9148 grm. of a solution, saturated, at  $20^\circ$ , gave 0.1719 grm.  $\text{BaSO}_4$ .

According to these determinations, the aqueous solution saturated at  $20^\circ$  contained the following percentages of the anhydrous salt: —

I.	II.
11.23	11.21

*Calcic Dibromacrylate*,  $\text{Ca}(\text{C}_3\text{HBr}_2\text{O}_2)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ . The calcium salt we prepared by neutralizing a solution of the acid with calcic carbonate. On cooling the concentrated solution, the salt separated in long radiating needles.

- I. 0.5625 grm. of the air-dried salt lost, when heated to  $100^\circ$ , 0.0668 grm.  $\text{H}_2\text{O}$ , and gave, when ignited with  $\text{H}_2\text{SO}_4$ , 0.1356 grm.  $\text{CaSO}_4$ .
- II. 0.3460 grm. of the salt lost at  $100^\circ$  0.0394 grm.  $\text{H}_2\text{O}$  and gave 0.0850 grm.  $\text{CaSO}_4$ .

Calculated for $\text{Ca}(\text{C}_3\text{HBr}_2\text{O}_2)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ .		Found.	
		I.	II.
Ca	7.13	7.09	7.22
$\text{H}_2\text{O}$	11.23	11.88	11.39

Fittig and Petri found in two determinations of water, in the calcium salt of their acid, the percentages 11.56 and 11.47, from which they calculate the formula with  $3\frac{1}{2}$  molecules of water given above.

The physical properties of the acid, and the analyses of the barium and calcium salts, leave no doubt of the identity of this dibromacrylic acid with that described by Fittig and Petri, although our results differ slightly in some respects from theirs. The acid from tribromsuccinic acid we have made only in sufficient quantity to assure ourselves that no qualitative differences are to be detected in the properties of the two acids, or in the habit of several of their salts.

*Iodbromacrylic Acid.*

Brompropionic acid dissolves readily in concentrated hydriodic acid, (b. pt. 127°) and so rapid is the action that in a few moments the solution is filled with crystals of the addition-product. The crude acid is pressed between folds of filter paper, and recrystallized from hot water.

The acid separates from a hot concentrated solution as an oil, but at a lower temperature it crystallizes in pearly scales, which melt at 110°. The acid is readily soluble in alcohol, ether, or chloroform, but sparingly in benzol, carbonic disulphide, or ligroin.

- I. 0.3800 grm. substance gave 0.1828 grm.  $\text{CO}_2$  and 0.0307 grm.  $\text{H}_2\text{O}$ .  
 II. 0.2945 grm. substance gave 0.4480 grm.  $\text{AgBr} + \text{AgI}$ .

Calculated for $\text{C}_3\text{H}_2\text{BrIO}_2$ .		Found.	
		I.	II.
C	12.99	13.12	
H	0.70	0.90	
Br } I }	74.73		74.47

The solubility of the acid in cold water we determined by neutralizing the saturated aqueous solution, made according to the method of V. Meyer with baric carbonate, and evaporating with sulphuric acid.

- I. 11.1382 grm. of a solution, saturated at 20°, gave 0.0785 grm.  $\text{BaSO}_4$ .  
 II. 10.8923 grm. of a solution, saturated at 20°, gave 0.0783 grm.  $\text{BaSO}_4$ .

According to these determinations, the aqueous solution of the acid saturated at 20° contained the following percentages:—

I.	II.
1.68	1.71

For the further characterization of the acid, we prepared the barium, calcium, and silver salts.

*Baric Iodbromacrylate*,  $\text{Ba}(\text{C}_3\text{HBrIO}_2)_2 \cdot 3\text{H}_2\text{O}$ . The barium salt we made by saturating the aqueous solution of the acid with baric carbonate and concentrating on the water bath. From concentrated solutions it crystallizes in fine needles; from more dilute, in rectangular plates. The air-dried salt contains three molecules of water, which it loses *in vacuo* over sulphuric acid.

- I. 0.4660 grm. of air-dried salt lost *in vacuo* over  $\text{H}_2\text{SO}_4$  0.0360 grm.  $\text{H}_2\text{O}$ , and lost then nothing at  $80^\circ$ .  
 II. 0.2832 grm. of air-dried salt lost *in vacuo* over  $\text{H}_2\text{SO}_4$  0.0208 grm.  $\text{H}_2\text{O}$ , and afterwards, when heated to  $80^\circ$ , 0.0011 grm.

Calculated for  $\text{Ba}(\text{C}_3\text{HBrIO}_2)_2 \cdot 3\text{H}_2\text{O}$ .

Found.

		I.	II.
$\text{H}_2\text{O}$	7.27	7.73	7.35

0.4427 grm. of the dried salt gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1498 grm.  $\text{BaSO}_4$ .

Calculated for  $\text{Ba}(\text{C}_3\text{HBrIO}_2)_2$ .

Found.

Ba	19.88	19.90
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The solubility of the salt in cold water we also determined.

- I. 2.0636 grm. of a solution saturated at  $20^\circ$  gave, on evaporation with  $\text{H}_2\text{SO}_4$ , 0.0967 grm.  $\text{BaSO}_4$ .  
 II. 3.0991 grm. of a solution saturated at  $20^\circ$  gave 0.1457 grm.  $\text{BaSO}_4$ .

From these determinations it follows that the aqueous solution, saturated at  $20^\circ$ , contains the following percentages of the anhydrous salt:—

I.	II.
13.86	13.90

*Calcic Iodbromacrylate*,  $\text{Ca}(\text{C}_3\text{HBrIO}_2)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ . The calcium salt resembles the barium salt closely in appearance, but is more soluble in water. The air-dried salt loses its crystal water completely *in vacuo* over sulphuric acid, or when heated to  $80^\circ$ .

- I. 0.7622 grm. of the air-dried salt lost 0.0771 grm.  $\text{H}_2\text{O}$  at  $80^\circ$ .  
 II. 0.7172 grm. of the air-dried salt lost 0.0698 grm.  $\text{H}_2\text{O}$  at  $80^\circ$ .

Calculated for  $\text{Ca}(\text{C}_3\text{HBrIO}_2)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ .

Found.

		I.	II.
$\text{H}_2\text{O}$	9.89	10.12	9.73

0.6518 grm. of the salt dried *in vacuo* gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1465 grm.  $\text{CaSO}_4$ .

Calculated for  $\text{Ca}(\text{C}_3\text{HBrIO}_2)_2$ .

Found.

Ca	6.76	6.61
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*Argentio Iodbromacrylate*,  $\text{AgC}_3\text{HBrIO}_2$ . The silver salt was precipitated from an aqueous solution of the acid by the addition of argentic nitrate. It formed short, clustered needles, which could be recrystallized from water, with but little decomposition.

- I. 0.4509 grm. of substance gave 0.1597 grm. AgCl and 0.0063 grm. metallic silver.  
 II. 0.7458 grm. substance gave, on precipitation with HBr, 0.3635 grm. AgBr.

Calculated for $\text{AgC}_3\text{HBrO}_2$ .		Found.	
		I.	II.
Ag	28.13	28.05	27.99

With hydrochloric acid, the addition takes place much more slowly; still, after long standing, the chlorbromacrylic acid is formed.

Of the products formed by the addition of halogens to brompropionic acid, we have thus far examined in detail only the tribromacrylic, although we have also made the diiodbromacrylic by the addition of iodine.

#### *Tribromacrylic Acid.*

Tribromacrylic acid may easily be made by adding slowly a slight excess of bromine to an aqueous solution of brompropionic acid. The color of the bromine gradually disappears, and the product of the reaction separates partially in the form of an oil. This oil gradually solidifies, and more of the same product can be extracted with ether from the aqueous solution. The resulting solid must be well pressed out, and may then be recrystallized from chloroform, or, better, from benzol. Thus prepared, it forms colorless, oblique prisms, which are very soluble in ether or alcohol, less soluble in cold chloroform or benzol, readily in hot, and soluble in carbonic disulphide or ligroin. It is but sparingly soluble even in boiling water. Melting point,  $118^\circ$ .

- I. 0.3449 grm. of the acid gave 0.1428 grm.  $\text{CO}_2$  and 0.0183 grm.  $\text{H}_2\text{O}$ .  
 II. 0.1782 grm. substance gave 0.3229 grm. AgBr.  
 III. 0.1433 grm. substance gave 0.2625 grm. AgBr.

Calculated for $\text{C}_3\text{HBr}_3\text{O}_2$ .		Found.		
		I.	II.	III.
C	11.65	11.29		
H	0.32	0.59		
Br	77.67		77.13	77.94

The acid when boiled with an excess of baric hydrate is hardly affected, although it is slowly decomposed by a boiling alcoholic solution of potassic hydrate. We have as yet isolated no products of this decomposition.

The solubility of the acid in water at ordinary temperatures we have also determined by the method of V. Meyer.

- I. 11.4429 grm. of a solution, saturated at  $20^{\circ}$ , gave, after neutralization with  $\text{BaCO}_3$  and evaporation with  $\text{H}_2\text{SO}_4$ , 0.0597 grm.  $\text{BaSO}_4$ .
- II. 12.7846 grm. of a solution, saturated at  $20^{\circ}$ , gave 0.0643 grm.  $\text{BaSO}_4$ .

According to these determinations, the aqueous solution of the acid saturated at  $20^{\circ}$  contains the following percentages:—

I.	II.
1.38	1.33

*Baric Tribromacrylate*,  $\text{BaC}_3\text{Br}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ . The barium salt we made by neutralizing the acid with a solution of baric hydrate. On cooling the concentrated solution, it crystallizes in long needles, which effloresce over sulphuric acid.

- I. 0.7888 grm. of the air-dried salt lost over  $\text{H}_2\text{SO}_4$  0.0532 grm.  $\text{H}_2\text{O}$ .
- II. 0.7585 grm. of the air-dried salt lost *in vacuo* over  $\text{H}_2\text{SO}_4$  0.0506 grm.  $\text{H}_2\text{O}$ .
- III. 0.4900 grm. of the air-dried salt lost at  $80^{\circ}$  0.0324 grm.  $\text{H}_2\text{O}$ .
- IV. 0.7024 grm. of the anhydrous salt gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.2185 grm.  $\text{BaSO}_4$ .
- V. 0.4486 grm. of the anhydrous salt gave 0.1398 grm.  $\text{BaSO}_4$ .

Calculated for $\text{Ba}(\text{C}_3\text{Br}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ .		Found.		
		I.	II.	III.
$\text{H}_2\text{O}$	6.68	6.75	6.67	6.61
Calculated for $\text{Ba}(\text{C}_3\text{Br}_3\text{O}_2)_2$ .		Found.		
		IV.	V.	
Ba	18.20	18.29	18.32	

The solubility of this salt in cold water was determined by the method of V. Meyer.

- I. 3.2130 grm. of a solution saturated at  $20^{\circ}$  left, on evaporation with  $\text{H}_2\text{SO}_4$  and ignition, 0.2349 grm.  $\text{BaSO}_4$ .
- II. 2.9600 grm. of a solution saturated at  $20^{\circ}$  gave 0.2170 grm.  $\text{BaSO}_4$ .

The aqueous solution saturated at  $20^{\circ}$  therefore contained the following percentages of the anhydrous salt:—

I.	II.
23.62	23.69

*Calcic Tribromacrylate*  $\text{Ca}(\text{C}_3\text{Br}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ . The calcium salt was made by warming the acid with water and calcic carbonate. It crys-

tallized in needles which were permanent in the air, but lost in weight over sulphuric acid.

- I. 0.4924 grm. of the air-dried salt lost at  $80^{\circ}$  0.0099 grm.  $\text{H}_2\text{O}$ .
- II. 0.8678 grm. of the air-dried salt lost at  $80^{\circ}$  0.0248 grm.  $\text{H}_2\text{O}$ .
- III. 0.4794 grm. of the anhydrous salt gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1001 grm.  $\text{CaSO}_4$ .
- IV. 0.8266 grm. of the anhydrous salt gave, on ignition with  $\text{H}_2\text{SO}_4$ , 0.1707 grm.  $\text{CaSO}_4$ .

Calculated for $\text{Ca}(\text{C}_2\text{Br}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ .		Found.	
		I.	II.
$\text{H}_2\text{O}$	2.67	2.01	2.86

Calculated for $\text{Ca}(\text{C}_2\text{Br}_3\text{O}_2)_2$ .		Found.	
		III.	IV.
Ca	6.10	6.14	6.07

*Argentio Tribromacrylate*,  $\text{AgC}_3\text{Br}_3\text{O}_3$ . The silver salt is precipitated when argentic nitrate is added to an aqueous solution of the acid, but is more readily prepared from a solution of the acid in diluted alcohol. The salt is tolerably stable, and crystallizes in small, six-sided plates.

0.5267 grm. of the salt gave 0.1848 grm.  $\text{AgCl}$ .

Calculated for $\text{AgC}_3\text{Br}_3\text{O}_3$ .		Found.
Ag	25.96	26.40

Mr. Mabery has undertaken the study of the chlorbromacrylic and diiodbromacrylic acid, and will present the results of these investigations in a separate paper.

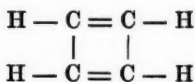
#### THEORETICAL CONSIDERATIONS.

Schmelz and Beilstein,\* from a comparison of the formula of melitic acid,  $\text{C}_4\text{H}_2\text{O}_4$  (as it was then written), with that of mucobromic acid,  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_3$ , were led to suspect a close connection between the two; but their investigations undertaken with the hope of proving this point yielded negative results.

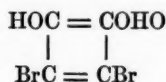
In 1869, Limpricht † suggested that a series of compounds, among which were furfural and its derivatives, contained a ring of four carbon atoms, and that they were therefore derived from an hypothetical hydrocarbon, —

\* Ann. Chem. u. Pharm., Suppl. iii. 280.

† Berichte der deutsch. chem. Gesellsch., ii. 212.



just as the various compounds of the aromatic series were derived from benzol. As the formula which naturally suggested itself for mucobromic acid he gives, —



although I am at a loss to know precisely how this formula is to be interpreted. This hypothesis received temporary support from the discovery of the so-called tetraphenol by Limpricht and Rohde; \* but further experiments made in Limpricht's laboratory failed to sustain it, and in the subsequent detailed account of these investigations † no allusion is made to it. In this paper Limpricht described the formation of fumaric acid by the action of bromine and water upon pyromucic acid, as well as the substance  $\text{C}_4\text{H}_4\text{O}_6$ , which he called fumaric acid aldehyde, and regarded as the product from which mucobromic acid was derived by substitution. In 1877 Baeyer ‡ showed that this latter substance was in fact the half-aldehyde of fumaric acid, in that it could be converted into fumaric acid by the action of argentic oxide. At the same time he pointed out the difficulty of supposing that mucobromic acid, which empirically was a substitution-product from this aldehyde, could be formed from it by the direct action of bromine.

In 1878, Wallach and Bischoff § published a paper upon the action of alkalis upon the  $\beta$  dichloracrylic acid, which Wallach ¶ had previously made by the reduction of chloralid. In a subsequent paper || upon the same subject, they assumed that the structure of the dibromacrylic acid from mucobromic, which O. R. Jackson and I \*\* had shortly before described in a preliminary notice, was established quite surely by its ready conversion into malonic acid, and Wallach was therefore led to append a note containing a suggestion which he had previously

\* Berichte der deutsch. chem. Gesellsch., iii. 90.

† Ann. Chem. u. Pharm., clxv. 278.

‡ Berichte der deutsch. chem. Gesellsch., x. 1362.

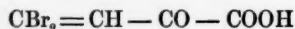
§ Ibid., xi. 751.

¶ Ibid., viii. 1580.

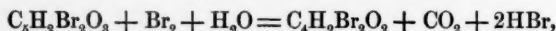
|| Ibid., xii. 57.

\*\* Ibid., xi. 1671.

made, that the constitution of mucobromic acid was probably represented by the formula, —



In 1879, Toennies,\* in investigating the action of bromine upon dibrompyromucic acid † in Baeyer's laboratory, found that a substance,  $\text{C}_4\text{H}_2\text{Br}_2\text{O}_2$ , was formed according to the equation, —

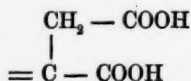


and that this could readily be converted into mucobromic by oxidation. This mode of formation led Toennies to the conclusion that mucobromic acid was the half-aldehyde of dibromfumaric acid. Further investigation in this direction Toennies relinquished in order to avoid interference with my work.

At the time of the publication of this paper by Toennies, my own experiments had shown that this view was in part correct. The conversion of mucobromic acid by the action of argentic oxide or other oxidizing agents into the dibrommaleic acid of Kekulé showed with sufficient precision that it was the half-aldehyde of this acid. On the other hand, it was evident that the dibrommaleic acid itself did not belong to the fumaric series, as could fairly be inferred from its mode of preparation; but that it was in reality a substituted maleic acid, since it could be carried unchanged through its anhydride.

A more direct proof of this fact was furnished by the discovery by Bandrowski ‡ of an isomeric acid of higher melting point, which could be converted into this by distillation.

Although it cannot be said that the constitution of fumaric and maleic acids is definitely established, the brilliant researches recently published from Fittig's laboratory leave but little doubt that the formula of maleic acid is, —



If this view of its structure be adopted, the structure of mucobromic acid must be represented by one of the formulæ, —

\* Berichte der deutsch. chem. Gesellsch., xii. 1202.

† Ibid., xi. 1088.

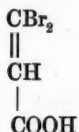
‡ Ibid., xii. 1232.



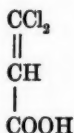


The ease with which it is decomposed, even in the cold, by alkalis and the aldehyde group thus converted into formic acid, would possibly incline one to adopt the first of these formulæ.

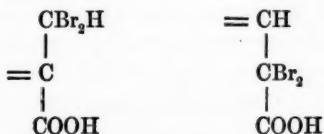
Unfortunately, no independent evidence concerning the position of the bromine atoms can as yet be drawn from the constitution of the dibromacrylic acid, which is formed at the same time, since none of its reactions give a clew to its structure. It may only be asserted, with tolerable certainty, that its formula is not, —



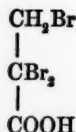
since the corresponding chlorinated acid made from mucochloric acid appears to be essentially different from the dichloracrylic acid of Wallach, and the formation of the latter from chloralid shows its formula to be, —



If the structure of mucobromic acid is represented by one of the formulæ given above, it follows that the dibromacrylic acid obtained from it has one of the forms, —

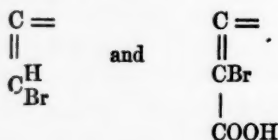


The formation of a tribrompropionic acid, melting at 116–117° by the addition of hydrobromic acid, would in itself be a sufficient reason for rejecting the second formula, if the structure of the tribrompropionic acid, melting at 92°, could be shown to be, —

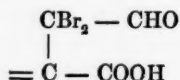


Although this is the constitution assigned to it by Michael and Norton,\* it is evident that this formula is based upon a pure assumption concerning the structure of the  $\alpha$  monobromacrylic acid from which it is made.

No more decisive arguments against the second formula can be drawn from the reactions or the derivatives of the dibromacrylic acid, although the formation of malonic acid follows more simply from the first formula, and the forms, —



which the second formula renders necessary for bromacetylen and brompropionic acids, seem hardly in its favor. It would therefore seem probable that the structure of mucobromic acid is, —



The close connection between the disubstituted acrylic acids derived from mucobromic and mucochloric acids and maleic acid makes their further study extremely desirable, more especially in order to obtain additional evidence bearing upon the position of the halogen atoms. Investigations in this direction are now in progress in this laboratory.

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\* Amer. Chem. Journ., ii. 18.

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## X.

ON THE PHOSPHOROGRAPH OF A SOLAR SPECTRUM,  
AND ON THE LINES IN ITS INFRA-RED REGION.

BY JOHN WILLIAM DRAPER, M.D.

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I PROPOSE in this communication to consider: 1. The peculiarities of a phosphorograph of the solar spectrum as compared with a photograph of the same object; 2. The antagonization of effect of rays of higher by those of lower refrangibility.

There is a striking resemblance between a photograph of that spectrum taken on iodide of silver and a phosphorograph taken on luminous paint, and other phosphorescent preparations. There are also differences.

## I. DESCRIPTION OF THE PHOTOGRAPHIC SPECTRUM.

In 1842, I obtained some very fine impressions of the first kind (on iodide of silver), and described them in the "Philosophical Magazine" (November, 1842), and again in February, 1847. One of these was made the subject of an elaborate examination by Sir J. Herschel. His description and explanatory views of it may be found in that journal, February, 1843.

From these it appears that such a photograph, *taken in presence of a weak extraneous light*, may be considered as presenting three regions.

1. A middle one extending from the boundary of the blue and green to a little beyond the violet; in this region the argentic iodide is blackened. 2. Below this, and extending from the boundary of the blue and green to the inferior theoretical limit of the prismatic spectrum, is a region strongly marked in which the action of the daylight has been altogether arrested or removed, the daylight and the sunlight having apparently counterbalanced and checked each other. 3. A similar protected region occurs beyond the violet. This, however, is very much shorter than the preceding. The sketch annexed to Herschel's paper represents these facts as well as they can be by an uncolored drawing.

## II. DESCRIPTION OF THE PHOSPHOROGRAPHIC SPECTRUM.

In a phosphorograph on luminous paint, the same general effects appear. If the impression of the spectrum be taken in the absence of extraneous light, there is a shining region corresponding to the blackened region of the photograph. But if, previously or simultaneously, extraneous light be permitted to be present, new effects appear. The shining region of the phosphorograph has annexed to it, in the direction of the less refrangible spaces and extending toward the theoretical limit of the spectrum, a region of blackness in striking contrast to the surrounding luminous surface. This blackness is, however, broken at a distance below the red by a luminous rectangle of considerable width. This occupies the space, and indeed arises from the coalescence of the bands  $\alpha$ ,  $\beta$ ,  $\gamma$ , discovered by me in 1842. It may be separated into its constituent bands, which are very discernible when registered on gelatine as presently described. And since this is not so easily done with the upper lines of the spectrum, we may infer that these are very much broader than the Fraunhofer lines, a result strengthened by the fact that these dark intervals can be more easily recognized by the thermopile than those lines. The blackness is then resumed. It extends to a short distance, and there the phosphorographic impression comes to an end.

This shining rectangle has long been known to students of phosphorescence, but its interesting origin has not until now been explained.

But more, just beyond the region of the violet, the same kind of action occurs, — a dark space, which, however, is of very much less extent than that beyond the red.

The photograph and the phosphorograph thus present many points of similarity. But though there are these striking points of resemblance, there are also striking differences.

In a spectrum four or five centimetres long, though the photograph may be crossed by hundreds of Fraunhofer lines, not one is to be seen in the phosphorograph, except those just referred to. The spectrum must be dispersed much more before they can be discerned.

## III. OF THE PROPAGATION OF PHOSPHORESCENCE FROM PARTICLE TO PARTICLE.

The explanation of this disappearance of the Fraunhofer lines is obvious. A phosphorescing particle may emit light enough to cause others in its neighborhood to shine, and each of these in its turn may

excite others, and so the luminosity may spread. In a former memoir I examined this in the case of chlorophane, and concluded that in that substance such a communication does not take place. But now, using more sensitive preparations, as follows, I have established in a satisfactory manner that it does.

The test plate referred to in the next paragraph was thus made. A piece of glass was smoked on one side in a flame, until it became quite opaque. When cool a few letters or words were written on it. Some photographic varnish was poured on it and drained. This, drying quickly, gave a black surface which could be handled without injury.

A phosphorographic tablet was made to shine by exposure to the sky. It was then carried into a dark room, and the test plate laid upon it. On the test plate another non-shining phosphorographic tablet was laid, and kept in that position a few minutes; then, on lifting this from the test plate, the letters were plainly visible, especially if it were laid on a piece of hot metal. So the light radiating from the first tablet through the letters of the test could produce phosphorescence in the second tablet, through glass more than a millimetre thick.

This lateral illumination is therefore sufficient to destroy the impression that is left by the fixed lines, unless indeed their breadth be sufficiently exaggerated, and as short an interval as possible permitted between the moment of insolation and that of observation.

It has been remarked that a photograph taken from a phosphorograph is never sharp. It looks as if it were taken out of focus, and this even though it may be a copy by contact. The light has spread from particle to particle. Under such circumstances, sharpness is impossible, because the phosphorograph itself is not sharp.

For this reason, also, the bright rectangle in a phosphorograph of the solar spectrum, arising from the coalescence of the infra-red lines  $\alpha$ ,  $\beta$ ,  $\gamma$ , is never sharp on its edges. It seems as if it were fading away on either side. It is also broader than would correspond to the actual position and width of those lines, and, particularly, it is somewhat rounded at its corners.

If we could obtain a thermograph of the solar spectrum, it would correspond very closely to the phosphorograph. The particles heated would radiate their heat to adjacent ones. Nothing like sharpness of definition could be obtained, except in very brief exposures before the effect had had time to spread.

#### IV. EXAMINATION OF PHOSPHORESCENT TABLETS BY GELATINE PHOTOGRAPHY.

The examination of a phosphorescent surface can be made now in a much more satisfactory manner than formerly. The light we have to deal with, being variable, declines from the moment of excitation to the moment of observation. And, though the phosphori now prepared are much more sensitive and persistent than those formerly made, they must still be looked upon as ephemeral. To examine them properly, the eye must have been a long time in darkness to acquire full sensitiveness.

It was recommended by Dufay to place a bandage over one eye that its sensitiveness might not be disturbed, whilst the other being left naked could be used in making the necessary preparations. But this on trial will be found, though occasionally useful, on the whole an uncomfortable and unsatisfactory method.

The exceedingly sensitive gelatine plates now obtainable remove these difficulties. The light emitted by blue phosphori, such as luminous paint, consists largely of rays between H and G, and these are rays which act at a maximum on the gelatine preparation. So if a gelatine plate be laid on a shining blue phosphorus it is powerfully affected, and any mark or image that may have been impressed on the phosphorus will on development in any of the usual ways be found on the gelatine. The gelatine has no need to wait after the manner of the eye. It sees the phosphorus instantly. It is impressed from the very first moment, and whilst the eye is accommodating itself and so losing the best of the effect, the gelatine is gathering every ray and losing nothing. Moreover, the effect upon it is cumulative. The eye is affected by the intensity of the emitted light, the gelatine by its quantity. Each moment adds to the effect of the preceding. The gelatine absorbs all the light that the phosphorus emits from the moment of excitation, or by suitable arrangement any fractional part thereof. It has another most important advantage. The phosphorus is yielding an ephemeral result, and is momentarily hastening to extinction, so that for a comparison of such a result with others of a like kind the memory must be trusted to. But the gelatine seizes it at any predetermined instant and keeps it forever. These permanent representations can at any future time be deliberately compared with one another.

To these still another advantage may be added. Very frequently an impression is much more perceptible on a gelatine copy than it is

on the phosphorus from which that copy was taken. This arises from the fact that the eye is made less sensitive by the light emitted from surrounding phosphorescent parts, and cannot perceive a sombre point or line among them. That is a physiological effect. But a gelatine copy in no respect dazzles or enfeebles the eye. For this reason, for instance, we may not be able in a phosphorograph to resolve visually the infra-red bright rectangle into its constituent lines, but we recognize them instantly in the gelatine.

I have made use of sensitive gelatine plates ever since their quality of being affected by phosphorescent light was announced by Messrs. Warnecke and Darwin. The more sensitive of these plates receives a full effect by an exposure of less than one minute.

But all kinds of phosphori will not thus affect a photographic tablet: there must be a sympathy between the phosphorescent and the photographic surfaces. Thus a phosphorus emitting a yellow light will not affect a photographic preparation which requires blue or indigo rays. This principle I detected many years ago. In my memoir on phosphorescence (*Phil. Mag.*, February, 1851), it will be seen that the green light emitted by chlorophane could not change the most sensitive photographic preparation at that time known — the daguerreotype plate — and hence I was obliged, in measuring the light it emits, to resort to Bouguer's optical method. The result would have turned out differently had the light to be measured been more refrangible, blue or indigo or violet.

A photographic surface agrees with the retina in this, that it has limits of sensitiveness. The eye is insensible to rays of much lower refrangibility than A, and much higher than H. Gelatine cannot perceive rays lower than F, but it is affected by others far higher than H. There is therefore a range for each, having its limits and also its place or point of maximum sensitiveness. But some substances, such as the iodide and bromiodide of silver, under special methods of treatment are affected either positively or negatively throughout the entire range of the spectrum.

In experiments for obtaining quantitative results, it should be borne in mind that there is generally a loss of effect. Between the moment of insolation and that of perception, either by the eye or by gelatine, emitted light escapes. The moment of maximum emission is the moment of completed insolation, and from this the light rapidly declines. It is necessary, therefore, to make that interval between the two moments as short as possible.



## V. OF THE EXTINCTION OF PHOSPHORESCENCE BY RED LIGHT.

I turn now to an examination of those parts of the phosphorographic spectrum from which the light has been removed. They are from the line F to the end of the infra-red space, and again for a short distance above the violet. The effect resembles the protecting action in the same region of a photograph.

Now, if similar effects are to be attributed to similar causes, we should expect to find in the photograph and phosphorograph the manifestation of a common action.

Several different explanations of the facts have been offered. Herschel suggested that the photograph might be interpreted on the optical principle of the colors of thin films. Very recently Captain Abney has attributed the appearance of the lower space to oxidation. But this can scarcely be the case in all instances. Mr. Claudet showed, in a very interesting paper on the action of red light, that a daguerreo-type plate can be used again and again by the aid of a red glass, and that the sensitive film undergoes no chemical change. (*Phil. Mag.*, February, 1848).

It was known to the earliest experimenters on the subject that if the temperature of a phosphorescent surface be raised, the liberation of its light is hastened, and it more quickly relapses into the dark condition. In the memoir to which I have previously referred (*Phil. Mag.*, February, 1851), I examined minutely into this effect of heat, and determined the conditions which regulate it. And since, on the old view of the constitution of the solar spectrum, the heat was supposed to increase toward the red ray, and when flint-glass or rock salt-prisms are employed to give its maximum far beyond that ray, it was supposed that this heat expelled the light, and consequently in all those parts of the phosphorus on which it fell the surface became dark through the expulsion or exhaustion of the light.

I speak of this as "the old view," because, as I have elsewhere shown, the curves supposed to represent heat, light, and actinism so called, have in reality nothing to do with those principles. They are merely dispersion curves having relation to the optical action of the prism and to the character of the surface on which the ray falls. (*Phil. Mag.*, August, 1872, December, 1872.)

But this heat explanation of the phosphorescent facts cannot be applied to the photographic. Nothing in the way of hastened or secondary radiation seems to take place in that case.

In phosphorescence the facts observed in the production of this



blackness are these. If a shining phosphorescent surface be caused suddenly to receive a solar spectrum, it will instantly become brighter in the region of the less refrangible rays, as will plainly appear on the spectrum being for a moment extinguished by shutting off the light that comes into the dark room to form it. If the light be re-admitted again and again, the like increase of brilliancy may again and again be observed, but in a declining way. Presently, however, the region that has thus emitted its light begins to turn darker than the surrounding luminous parts. If now we no longer admit any spectrum light, but watch the phosphorescent surface as its luminosity slowly declines, the region that has thus shot forth its radiation becomes darker and darker, and at a certain time quite black. The surrounding parts in the course of some hours slowly overtake it, emitting the same quantity of light that had previously been expelled from it, and eventually all becomes dark.

Now, apparently, all this is in accordance with the hypothesis of the expulsion of the light by heat. There are, however, certain other facts which throw doubt on the correctness of that explanation.

On that hypothesis, the darkening ought to begin at the place of maximum heat, that is, when flint glass apparatus is used, below the red ray, and from this it should become less and less intense in the more refrangible direction. But, in many experiments carefully made, I have found that the maximum of blackness has its place of origin above the line D, and indeed where the orange and green rays touch each other. Not infrequently, in certain experiments the exact conditions of which I do not know and cannot always reproduce, the darkening begins at the upper confines of the green, and slowly passes down to beyond the red extremity; that is to say, its propagation is in the opposite direction to that which it ought to show on the heat hypothesis.

Still more, as has been stated, there is a dark space above the violet. Now it is commonly held that in this region there is little or no heat. If so, what is it that has expelled or destroyed the light?

The experiments above referred to I made with the recently introduced luminous paint. It presented the facts under their simplest form. But I have also tried many other samples, for which I am indebted to the courtesy of Professor Barker of Philadelphia. Among them I may mention as being very well known the specimens made by Dubosc, enclosed in flat glass tubes, contained in a mahogany case, and designed for illustrating the different colored phosphorescent lights emitted. They are to be found in most physical cabinets.

These, however, do not show the facts in so clear a manner. On receiving the impress of a solar spectrum they present patches of light and shade irregularly distributed. Though in a general way they confirm the statements made above, they do not do it sharply or satisfactorily.

Dubosc's specimens to which I have had access are enumerated as follows: 1. Calcium violet; 2. Calcium blue; 3. Calcium green; 4. Strontium green; 5. Strontium yellow; 6. Calcium orange. Restricting my observation to the space beyond the red, — which, as has been said, presents a bright rectangle in the darkness, about as far below the red as the red is below the yellow, — I found that this rectangle is not given by 1 and 2. In 3 it is doubtful. In 4 it is quite visible, and in 5 and 6 strikingly so.

Is the blackening then due to heat? That it occurs beyond the violet, that is, beyond the lines H, seems to render such an opinion doubtful, for it is commonly thought that the effect of heat is not recognizable there. And in the phosphorogenic spectroscopie I have used, the optical train, prism, lenses, &c., is of glass, which must of course exercise a special selective heat-absorption; but the traces of this in the phosphorograph I could never detect.

In the diffraction spectrum, I had attempted nearly forty years ago to ascertain the distribution of heat (Phil. Mag., March, 1857), but could not succeed with the experiment in a completely satisfactory manner, so small is the effect. I exposed a tablet of luminous paint to such a diffraction spectrum formed by a reflecting grating, having 17,296 lines to the inch, and was not a little surprised to see that from the blue to the red end of the spectrum there is an energetic extinction of the light, and darkness is produced. I repeated this with other gratings, and under varied circumstances, and always found the same effect.

Now, considering the exceedingly small amount of heat available in this case, and considering the intensity of the effect, is there not herein an indication that we must attribute this result to some other than a calorific cause?

I endeavored to obtain better information on this point by using the rays of the moon, which, as is well known, are very deficient in heating power. Many years ago I had obtained some phosphorographs of that object. With the more sensitive preparations now accessible, and with a telescope 11 inches in aperture and 150 inches focus, there was no difficulty in procuring specimens about 1.4 inch in diameter. These represented the lunar surface satisfactorily. At half-moon an

exposure of three or four seconds was sufficient to give a fair proof. But, on insulating a phosphorescent tablet, and causing the converging moon rays to pass through the red glass which I commonly use as an extinguisher, no effect was produced by the red moonlight on the shining surface.

I repeated this experiment using a lens 5 inches in diameter and 7 inches focus so arranged that the moon's image could be kept stationary on the phosphorescent tablet. That image was about  $\frac{1}{4}$  inch in diameter. Then, insulating the tablet, the moon rays, after passing through a red glass, were caused to fall upon it. The exposure continued ten minutes, but no effect was produced on the shining surface. The lunar image was so brilliant that when the red glass was removed, and a non-shining phosphorescent surface was exposed to it, a bright image could be produced in a single second.

But in order to remove the effect of the more refrangible rays by the less, the latter must not only have the proper wave length but also the proper amplitude of vibration. This principle applies both to photographic and phosphorographic experiments. In my memoir on the negative or protecting rays of the sun (*Phil. Mag.*, February, 1847) it is said, "Before a perfect neutralization of action between two rays ensues, those rays must be adjusted in intensity to each other." It requires a powerful yellow ray to antagonize a feeble daylight.

It is owing to the difference in amplitude of vibration that the heat of radiation seems so much more effective than the heat of conduction. A temperature answering to that of the boiling point of mercury must be applied to a phosphorescent tablet for quite a considerable time before all the light is extinguished. But the red end of the spectrum and that even of the diffraction spectrum, in which the heat can with difficulty be detected by the most sensitive thermometer, accomplishes it very quickly.

#### VI. OF THE INFRA-RED LINES OR BANDS IN THE SUN'S SPECTRUM.

At a distance about as far below the red as the red is below the yellow in the solar spectrum, I found in 1842, in photographs taken on iodide of silver (Daguerre's preparation), three great lines or bands, with doubtful indications of a fourth still further off. I designated them as  $\alpha$ ,  $\beta$ ,  $\gamma$ , and published an engraving of them in the *Philosophical Magazine* for May, 1843.

In 1846, MM. Foucault and Fizeau having repeated the experi-

ment, thus originally made by me, presented a communication to the French Academy of Sciences. They had observed the antagonizing action above referred to, and had seen the infra-spectral lines  $\alpha$ ,  $\beta$ ,  $\gamma$ . They had taken the precaution to deposit with the Academy a sealed envelope, containing an account of their discovery, not knowing that it had been made and published long previously in America.

Sir J. Herschel had made some investigations on the distribution of heat in the spectrum, using paper blackened on one side and moistened with alcohol on the other. He obtained a series of spots or patches, commencing above the yellow and extending beyond the red. Some writers on this subject have considered that these observations imply a discovery of the lines  $\alpha$ ,  $\beta$ ,  $\gamma$ . They forget, however, that Herschel did not use a slit, but the image of the Sun, — an image which was more than a quarter of an inch in diameter. Under such circumstances, it was impossible that these or any other of the fixed lines could be seen.

I have many times repeated this experiment, but could not obtain the same result, and therefore attributed my want of success to unskillfulness. More recently Lord Rayleigh (*Phil. Mag.*, November, 1877), having experimented in the same direction, seems to be disposed to attribute these images to a misleading action of the prism employed. Whatever their cause may be, it is clear that they have nothing to do with the fixed lines  $\alpha$ ,  $\beta$ ,  $\gamma$ , now under consideration.

In these experiments, and also in others made about the same time on the distribution of heat in the spectrum, I attempted to form a diffraction spectrum without the use of any dioptric media, endeavoring to get rid of all the disturbances which arise through the absorptive action of glass by using as the grating a polished surface of steel on which lines had been ruled with a diamond, and employing a concave mirror instead of an achromatic lens; and, though my results were imperfect and incomplete, I saw enough to convince me that it is absolutely necessary to employ a spectrum that has been formed by reflection alone. (*Phil. Mag.*, March, 1857, p. 155.)

In 1871, M. Lamanski succeeded in detecting these lines or bands by the aid of a thermomultiplier. He was not adequately informed on what had already been done in the matter in America, for he says that "with the exception of Foucault and Fizeau, in their well-known experiments on the interference of heat, no one as yet has made reference to these lines." Nearly thirty years before the date of his memoir I had published an engraving of them. (*Phil. Mag.*, May, 1843.)

After I had discovered these three lines, I intended to use the grat-

ing for the exploration of that region, since it extends it, far more than the prism can do; but, on making the attempt, was discouraged by the difficulty of getting rid of the more refrangible lines belonging to the second spectrum. I had hoped to eliminate these by passing the ray on its approach to the slit through a solution of the bichromate of potash. But the bichromate in long exposures permits a sufficiency of the more refrangible rays to pass, to produce a marked photographic effect; and hence I feared that any experiments supposed to prove the existence of lines in the infra-red would be open to the criticism that they, in reality, belonged to the more refrangible regions of the spectrum of the second order, and that a satisfactory examination of the case would exclude the use of the grating and compel that of the prism. With the prism I could not obtain clear evidence of the existence of more than three lines, or perhaps groups, and doubtful indications of a fourth. If in these examinations we go as far as wave length 10,750, the limit of Captain Abney's map, we nearly reach the line  $H^2$  of the third spectrum. This would include all the innumerable lines of spectrum 2, and even many of those of spectrum 3. In such a vast multitude of lines, how would it be possible to identify those that properly belonged to the first, and exclude those of the second and third spectra? Besides, do we not encounter the objection that this is altogether beyond the theoretical limit of the prismatic spectrum?

This brings us to Captain Abney's recent researches, which, by the aid of the grating, carry the investigation referred to the prismatic spectrum as far below the red as the red is below the yellow. They are not to be regarded as an extension of exploration in the infra-red region,—for they really do not carry us beyond my own observations in 1842,—but as securing the resolution of these lines or bands into their constituent elements. I had never regarded them as really single lines. The breadth or massiveness of their photographs, too, plainly suggests that they are composed of many associated ones. The principle of decreasing refrangibility with increasing wave length incapacitates the prism from separating them, but the grating which spreads them out according to their wave length reveals at once their composite character.

In Captain Abney's map, after leaving the red line A, we find three groups: (1) ranging from about 8150 to 8350; (2) from 8930 to 9300; (3) from 9350 to 9800. These, admitting that the lines of the subsequent grating spectra have been excluded, are then the resolution of  $\alpha$ ,  $\beta$ ,  $\gamma$ .

I suppose that care has been taken to make sure of that, either by absorbent media or by a subsidiary prism. If the grating had been ruled in such a manner as to extinguish the second spectrum, inconveniences would arise from the characteristics thereby impressed on the first.

In the phosphorographic spectrum on luminous paint, this vast multitude of lines is blended into a mass which probably can never be completely resolved into its elements, on account of the propagation of phosphorescence from particle to particle. I have resolved it into two or three constituent groups, and frequently have seen indications of its capability of its resolution into lines, in the serrated aspect of its lateral edges.

I believe that luminous paint enables us to approach very nearly, if not completely, to the theoretical limit of the prismatic spectrum.

The history of these interesting infra-red lines is briefly this. They were discovered by me in 1842, and an engraving and description of them given in the "Philosophical Magazine." They were next seen by Foucault and Fizeau in 1846, and a description of them presented to the French Academy of Sciences. They were again detected by Lamanski with the thermopile in 1871. Their resolution into a great number of finer lines was accomplished by Abney, who gave a Bakerian lecture describing them before the Royal Society in 1880. Finally, they have been redetected by me in the shining rectangle, just above the theoretical limit of the prismatic spectrum, given by many phosphorescent substances.

UNIVERSITY OF NEW YORK  
Dec. 1, 1880.

## XI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.\*ON THE DIIODBROMACRYLIC AND CHLORBROM-  
ACRYLIC ACIDS.

BY C. F. MABERY AND RACHEL LLOYD.

Presented by H. B. HILL.

THE readiness with which brompropionic acid unites with the halogens and the haloid acids to form members of the acrylic acid series has been described by Prof. H. B. Hill,<sup>†</sup> and certain of these addition products have been studied in detail by him and one of us.<sup>‡</sup>

The products which result by the action of iodine and of hydrochloric acid on brompropionic acid will be described in this paper.

DIIIODBROMACRYLIC ACID,  $C_3I_2BrO_2H$ .

Diiodbromacrylic acid is formed when brompropionic acid is allowed to stand for some time with a solution of iodine in ether. As this method of preparation was found to be somewhat tedious from the length of time required to complete the reaction, we tried the effect of raising the temperature. Brompropionic acid, with a slight excess over the calculated weight of iodine and five parts by weight of ether, was heated for two hours under a return condenser on the water bath. The residue left after the evaporation of the ether was extracted with successive portions of warm water, and the solution concentrated by evaporation. Diiodbromacrylic acid was deposited from this solution, on cooling, in glistening plates, which were purified by recrystallization from hot water.

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\* This research was conducted in connection with the Summer Course of Instruction in Chemistry. C. F. M.

† Berichte der deutsch. chem. Gesellsch., 1879, p. 660.

‡ These Proceedings, p. 211.



The yield of pure product by this method has been about sixty per cent of the amount theoretically required. The mother liquors of the first crystallizations gave by evaporation an oily product, which solidified on standing, but which could be purified only with considerable difficulty. This substance crystallizes in flat, white, six-sided plates, very sparingly soluble in cold water, readily in hot, and very soluble in ether, alcohol, carbonic disulphide, and ligroin. It melts at  $160^{\circ}$ , and sublimes slowly at higher temperatures, apparently unchanged. A yellow coating is formed on the surface when it is exposed to the action of light, yet the decomposition by nitric acid in the estimation of the halogens is not complete below  $300^{\circ}$ .

The following results were obtained by analysis:—

0.5188 grm. substance gave 0.1682 grm.  $\text{CO}_2$  and 0.0180 grm.  $\text{H}_2\text{O}$ .

0.2004 grm. substance gave by Carius' method 0.3276 grm.  $\text{AgI} + \text{AgBr}$ .

	Calculated for $\text{C}_8\text{I}_2\text{BrO}_2\text{H}$ .	Found.
C	8.93	8.84
H	.25	.39
$\text{I}_2 + \text{Br}$	82.87	82.96

The solubility in cold water was determined by the method of V. Meyer. The filtered solution was neutralized with baric carbonate, evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

I. 11.7286 grm. solution gave 0.0707 grm.  $\text{BaSO}_4$ .

II. 13.3239 grm. solution gave 0.0793 grm.  $\text{BaSO}_4$ .

The solution, saturated at  $20^{\circ}$ , contains, therefore, the percentages:—

I.	II.
2.08	2.05

Hence diiodobromacrylic acid requires for solution 48.37 parts water at  $20^{\circ}$ .

#### SALTS OF DIHIOBROMACRYLIC ACID.

*Baric Diiodobromacrylate*,  $\text{Ba}(\text{C}_8\text{I}_2\text{BrO}_2)_2 \cdot 4\text{H}_2\text{O}$ . A solution of the acid was heated with an excess of baric carbonate, filtered, and concentrated by evaporation. The salt crystallized, on cooling, in flat prisms arranged in stellate groups. It is very soluble in hot, less soluble in cold, water.



- I. 0.8805 grm. air-dried salt gave 0.0638 grm.  $\text{H}_2\text{O}$  at  $80^\circ$ .  
 II. 0.8981 grm. air-dried salt gave 0.0629 grm.  $\text{H}_2\text{O}$  at  $80^\circ$ .  
 III. 0.8049 grm. anhydrous salt gave 0.2002 grm.  $\text{BaSO}_4$ .

Calculated for $\text{Ba}(\text{C}_8\text{I}_2\text{BrO}_2)_2 \cdot 4\text{H}_2\text{O}$ .		Found.	
		I.	II.
$\text{H}_2\text{O}$	7.11	7.24	7.00

Calculated for $\text{Ba}(\text{C}_8\text{I}_2\text{BrO}_2)_2$ .		Found.	
Ba	14.55		14.62

To determine the solubility in cold water, a hot solution was kept at  $20^\circ$  for four hours, with occasional stirring. The filtered solution was evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

- I. 3.2417 grm. solution gave 0.1218 grm.  $\text{BaSO}_4$ .  
 II. 7.0500 grm. solution gave 0.2665 grm.  $\text{BaSO}_4$ .

This solution contains, therefore, the following percentages:—

I.	II.
15.17	15.26

Taking the mean of these results, this salt requires for solution 6.571 parts water at  $20^\circ$ .

*Calcic Diiodbromacrylate*,  $\text{Ca}(\text{C}_8\text{I}_2\text{BrO}_2)_2$ . This salt was prepared by neutralizing a solution of the acid with calcic carbonate, and evaporating the filtered solution. The salt crystallizes in branching needles, which are very soluble in water.

0.5995 grm. of the air-dried salt lost 0.0031 grm. at  $80^\circ$ .

This was probably due to the presence of a trace of hygroscopic moisture.

0.5964 grm. of the salt, dried at  $80^\circ$ , gave 0.0945 grm.  $\text{CaSO}_4$ .

	Calculated for $\text{Ca}(\text{C}_8\text{I}_2\text{BrO}_2)_2$ .	Found.
Ca	4.74	4.66

*Argentie Diiodbromacrylate*,  $\text{AgC}_8\text{I}_2\text{BrO}_2$ . Argentie nitrate, added to a solution of the acid, caused a voluminous precipitate of the silver salt, which was washed and dried over sulphuric acid for analysis. It forms oblique prisms, very slightly soluble in cold water, but readily soluble in dilute nitric acid.

0.9585 grm. salt gave 0.2677 grm.  $\text{AgCl}$ .

	Calculated for $\text{AgC}_3\text{I}_2\text{BrO}_2$	Found.
Ag	21.17	21.02

*Potassic Diiodbromacrylate*,  $\text{KC}_3\text{I}_2\text{BrO}_2 \cdot 2\text{H}_2\text{O}$ . A solution of the acid was neutralized with potassic carbonate, and evaporated on the water bath. On cooling, the salt separated in the form of oblique prisms, which are quite soluble in water.

1.8818 grm. of the air-dried salt gave 0.1381 grm.  $\text{H}_2\text{O}$  at  $80^\circ$ .

1.7460 grm. anhydrous salt gave 0.3347 grm.  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{KC}_3\text{I}_2\text{BrO}_2 \cdot 2\text{H}_2\text{O}$	Found.
$\text{H}_2\text{O}$	7.55	7.33

	Calculated for $\text{KC}_3\text{I}_2\text{BrO}_2$	Found.
K	8.87	8.50

#### CHLORBROMACRYLIC ACID, $\text{C}_3\text{ClBrC}_2\text{H}_2$ .

Chlorbromacrylic acid may be made by the action of ordinary fuming hydrochloric acid on brompropionic acid. This reaction, however, takes place slowly in the cold; and, although the application of heat causes a more rapid formation of the chlorbromacrylic acid, it produces a secondary decomposition which renders the purification of the product somewhat difficult. We therefore tried the action of hydrochloric acid saturated at  $0^\circ$ . The acid solution soon became filled with crystals of the addition product; and after standing twenty-four hours the reaction was complete. The excess of hydrochloric acid was removed by decantation, and by pressure between folds of filter paper, and the chlorbromacrylic acid was purified by crystallization from hot water. It separates as an oily liquid from a hot aqueous solution; but when nearly cold it crystallizes, forming elongated, flat prisms or needles.

This acid melts at  $70^\circ$ , and sublimes quite freely at a somewhat higher temperature. It is much more soluble in hot than in cold water, and readily soluble in ether, alcohol, benzol, and carbonic disulphide. Its composition was determined by the following analyses:—  
0.4462 grm. substance gave 0.3126 grm.  $\text{CO}_2$  and 0.0337 grm.  $\text{H}_2\text{O}$ .  
0.1792 grm. substance gave, by the method of Carius, 0.3186 grm.

$\text{AgCl} + \text{AgBr}$ .

	Calculated for $\text{C}_3\text{ClBrC}_2\text{H}_2$	Found.
C	19.40	19.11
H	1.08	.84
Cl + Br	62.26	61.94

The solubility of this acid in cold water was determined by the same method as the diiodbromacrylic acid.

- I. 11.6861 grm. solution gave 0.4178 grm.  $\text{BaSO}_4$ .
- II. 14.4534 grm. solution gave 0.5264 grm.  $\text{BaSO}_4$ .

The solution, saturated at  $20^\circ$ , contains the percentages:—

I.	II.
5.69	5.80

The mean of these results gives 17.41 parts as the quantity of water required for solution at  $20^\circ$ .

#### SALTS OF CHLORBROMACRYLIC ACID.

The salts of this acid were made by the same methods as the corresponding salts of diiodbromacrylic acid.

*Baric Chlorbromacrylate*,  $\text{Ba}(\text{C}_3\text{ClBrO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$ . This salt crystallizes in flattened prisms, which belong apparently to the monoclinic system. Its composition was established by the following analyses:—

- I. 0.3730 grm. air-dried salt gave 0.0263 grm.  $\text{H}_2\text{O}$  at  $80^\circ$ .
- II. 0.6283 grm. air-dried salt gave 0.0437 grm.  $\text{H}_2\text{O}$  at  $80^\circ$ .
- III. 0.3467 grm. anhydrous salt gave 0.1606 grm.  $\text{BaSO}_4$ .
- IV. 0.4468 grm. anhydrous salt gave 0.2053 grm.  $\text{BaSO}_4$ .

Calculated for $\text{Ba}(\text{C}_3\text{ClBrO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$ .		Found.	
		I.	II.
$\text{H}_2\text{O}$	6.64	7.05	6.96
Calculated for $\text{Ba}(\text{C}_3\text{ClBrO}_2\text{H})_2$ .		Found.	
		III.	IV.
Ba	27.07	27.23	27.02

The solubility in cold water was determined by the method of V. Meyer.

- I. 2.8936 grm. solution gave 0.1914 grm.  $\text{BaSO}_4$ .
- II. 5.1385 grm. solution gave 0.3378 grm.  $\text{BaSO}_4$ .

From these results the following percentages were calculated:—

I.	II.
14.06	14.28

This salt, therefore, requires for solution 6.985 parts of water at  $20^\circ$ .

*Calcic Chlorbromacrylate*,  $\text{Ca}(\text{C}_3\text{ClBrO}_2\text{H})_2 \cdot 4\text{H}_2\text{O}$ . This salt forms branching needles, which are very soluble in hot, less soluble in cold, water.

- I. 0.4981 grm. air-dried salt gave 0.0762 grm.  $H_2O$  at  $80^\circ$ .  
 II. 0.6211 grm. air-dried salt gave 0.0956 grm.  $H_2O$  at  $80^\circ$ .  
 III. 0.4219 grm. anhydrous salt gave 0.1424 grm.  $CaSO_4$ .  
 IV. 0.5096 grm. anhydrous salt gave 0.1713 grm.  $CaSO_4$ .

Calculated for $Ca(C_3ClBrO_2H)_2 \cdot 4H_2O$ .		Found.	
		I.	II.
$H_2O$	14.97	15.30	15.39
Calculated for $Ca(C_3ClBrO_2H)_2$		Found.	
		III.	IV.
Ca	9.78	9.93	9.87

*Argentio Chlorbromacrylate*,  $Ag(C_3ClBrO_2H)_2$ . This salt was precipitated by the addition of argentic nitrate and ammoniac hydrate to a solution of the acid. It forms microscopic needles, which are almost insoluble in cold water.

- I. 0.2760 grm. salt gave 0.1337 grm.  $AgCl$ .  
 II. 0.3445 grm. salt gave 0.1668 grm.  $AgCl$ .

Calculated for $Ag(C_3ClBrO_2H)_2$ .		Found.	
		I.	II.
Ag	36.93	36.47	36.88

*Potassic Chlorbromacrylate*,  $KC_3ClBrO_2H$ . This salt forms clusters of irregular, pointed, anhydrous prisms, which are less soluble in cold than in hot water.

0.5346 grm. salt, dried at  $80^\circ$ , gave 0.2132 grm.  $K_2SO_4$ .

Calculated for $KC_3ClBrO_2H$ .		Found.
K	17.49	17.91

The addition of bromine to chlorbromacrylic acid takes place very readily at the ordinary temperature, with the formation of chlortribrompropionic acid. A solution of the acid in chloroform was allowed to stand several days, with somewhat more than the calculated weight of bromine. Chlortribrompropionic acid separated from this solution in large prismatic crystals, which after crystallization from carbonic disulphide melted at about  $98^\circ$ . This acid will be submitted to a more extended study.

## XII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

By C. LORING JACKSON.

TENTH PAPER.

THE RELATIVE CHEMICAL ACTIVITY OF CERTAIN SUBSTITUTED BENZYL BROMIDES.

Presented November 12, 1879

IN the following paper I have the honor of laying before the Academy an account of some experiments undertaken to compare the ease with which bromine can be removed from the side-chains of the substituted benzyl bromides described in the first paper of this series; in other words, an attempt to establish some relation between the structure of a molecule and its chemical activity. The differences in structure, which I have taken up, are of two sorts, — those depending on difference in the position of the same element, as in the three monobrombenzyl bromides; and those depending on the presence of different but related elements in the same position, as in parachlor-, parabrom-, and paraiodbenzyl bromide.

After a careful consideration of the reagents by which the side-chain bromine could be removed from these substances in a simple metathetical reaction, I decided that sodic acetate promised the best results, and, after many experiments, adopted a method, which consisted in treating equivalent amounts of the substituted benzyl bromides, for the same length of time and under the same conditions, with an alcoholic solution of sodic acetate, and determining by volumetric analysis the amount of sodic bromide formed from each according to the following general reaction, —



in which X stands for the halogen atom attached to the benzol ring. But even this reaction, although less full of sources of error than most of those available, is not so well adapted to work of this sort as I could wish; since the action takes place so rapidly that small differences in the time of two experiments produce comparatively large differences in their results. I have tried, therefore, to make the time occupied in starting and stopping the action as short as possible, and have reduced the duration of the addition of the sodic acetate solution, by which the reaction is started, to five seconds; but I have not been so successful in stopping the reaction promptly, as this was done by precipitating the organic matter with water, of which so large a quantity was needed that the average duration of the addition was fifteen seconds.

This method of stopping the reaction by means of water is not above criticism; for, although I consider of little or no weight the possible objection that the reaction may continue forming more sodic bromide after the addition of water, yet the presence of even a small amount of the substituted benzylbromide will cause a serious error in the determination of the sodic bromide,\* and it is very hard to remove this completely by filtration; that it is possible, however, if sufficient care is used, appears from the following experiment:—

A mixture of parabrombenzylbromide and parabrombenzylacetate was dissolved in a little alcohol, and, after precipitating with water and filtering, 4 c.c. of a standard solution of argentic nitrate added, upon titrating the liquid 5.3 c.c. of the standard solution of potassic sulphocyanate were found to be necessary, the theoretical quantity being 5.27 c.c.

In selecting a solvent, it was necessary to find one which would dissolve all the substances entering into the reaction; since Berthelot and Pean de St. Gilles† have shown that, when two liquids which do not mix are used, the amount of action depends to a large extent on the

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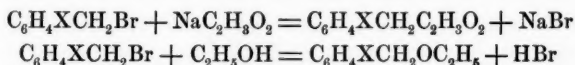
\* This point is illustrated by the following experiments: A little parabrombenzylbromide was dissolved in alcohol, and precipitated with water; 2.30 c.c. of a standard solution of argentic nitrate were added, and the mixture allowed to stand fifteen minutes; on titrating for silver, it was found that 0.41 c.c., corresponding to 0.0069 grm. of  $\text{AgNO}_3$ , had been lost, while another similar sample which stood for one hour and twenty minutes lost 1.59 c.c., corresponding to 0.026 grm. of  $\text{AgNO}_3$ .

† Ann. Chim. Phys., 3d ser., lxvi. p. 46; lxviii. p. 238.

size of the surface of contact; and therefore no constant results can be expected. I have confirmed these observations, while studying the action of water on the substituted benzylbromides, as will be described later in this paper. Under these circumstances, alcohol seemed to be the only solvent admissible; but its use introduced a new source of error, since it acts on the benzylbromides, forming the corresponding ethyl ethers and hydrobromic acid, as is shown by the following experiment.

Some parabrombenzylbromide was boiled with absolute alcohol for fifteen minutes. After removing the organic matter by precipitation with water and filtration, a precipitate was formed on the addition of argentic nitrate.

This defect was removed as completely as possible by taking pains that the benzylbromides should be in contact with the alcohol for the same length of time in each series of experiments. Then the results depended, in each case, on two reactions, viz. :—



but, as the time of each was the same in all the experiments of a series, the occurrence of the second did not materially affect the result, especially as the amount of substance entering into this second reaction was very small.

The adjustment of the amount of alcohol to be used was no easy matter, because sodic acetate and bromide are very sparingly soluble in absolute alcohol, and any considerable dilution interferes with the solubility of the benzylbromides; nor could the difficulty be removed by increasing to any great extent the amount of alcohol, as this would have increased the length of time necessary to stop the reaction.

More important than any of the sources of error yet mentioned is that proceeding from the differences in volatility of the benzylbromides with alcohol vapor, since this must alter the amount of substance capable of entering into the reaction in each case by the quantity of bromide volatilized with the alcohol in the upper part of the flask; and it is principally to this cause, which I could find no way of removing, that I am inclined to ascribe the considerable variations in my results.

This discussion of the defects in the process shows that no absolute agreement in the numbers obtained can be expected; but they agree nearly enough to establish certain interesting relations between the rates of decomposition of some of these compounds.

*Comparison of the Three Monobrombenzylbromides.*

One gramme of each substance was weighed in a wide-mouthed flask, the cork of which was fitted with a return-condenser and a short wide tube closed with a cork for the addition of the reagents, 10 c.c. of absolute alcohol were added, and the mixture heated for seven minutes in a boiling water-bath. After which, 25 c.c. of a saturated solution of sodic acetate in 99 per cent alcohol, at  $60^{\circ}$  to  $70^{\circ}$ , were introduced, and the flask heated for a definite time, varied in each series of experiments; care being taken that the water-bath boiled violently during the whole time, and that the three flasks to be compared were immersed to the same depth, and arranged symmetrically in the bath. The action was stopped by the addition of a large quantity of water, the flask being removed from the bath at the same time; and, after filtering out the organic matter, the quantity of sodic bromide formed by the reaction was determined by Volhard's \* excellent method of titration with sulphocyanate.

The brombenzylbromides used were made in the way described in the first paper † of this series, and purified with the utmost care.

The sodic acetate was prepared by drying the crystallized salt in an air-bath. It yielded on analysis the following result:—

0.7720 grm. of  $\text{NaC}_2\text{H}_3\text{O}_2$  gave 0.6655 grm. of  $\text{Na}_2\text{SO}_4$ .

	Calculated.	Found.
Sodium	28.05	27.93

The absolute alcohol did not turn anhydrous cupric sulphate blue, and neither it nor the acidified solution of the sodic acetate gave a precipitate with argentic nitrate.

The 25 c.c. of the alcoholic solution of sodic acetate contained a little more than enough of the salt to decompose the one gramme of brombenzylbromide used, since,—

10 c.c. of this solution yielded on evaporation 0.186 grm. of sodic acetate, and therefore,—

25 c.c. contained . . . . .	0.340 grm.
Needed for 1 grm. brombenzylbromide . .	0.328 grm.
Excess . . . . .	0.012 grm.

\* Ann. Chem. u. Pharm., exc. p. 1.

† These Proceedings, vol. xii. (n. s. iv.) p. 211.



The 35 cc. of alcohol present were much more than sufficient to dissolve all the sodic bromide formed, as a rough determination showed that, —

35 c.c. of absolute alcohol dissolve 0.627 grm. NaBr.

1 grm. brombenzylbromide yields 0.412 grm. NaBr.

All the substances, therefore, were in solution throughout the experiment.

The accuracy of the method was tested by the following experiments, in each of which two portions of parabrombenzylbromide were compared: —

I. Time, five minutes.

A. 1 gramme parabrombenzylbromide lost 0.1164 grm. Br.

B. " " " 0.1102 grm. Br.

Difference . . . . . 0.0062 grm. Br.

	Percentage of total side-chain bromine removed.	B in per cent of A.
A.	36.39	100.0
B.	34.47	94.7
	<u>1.92</u>	<u>5.3</u>

II. Time, seven minutes.

A. 1 grm. parabrombenzylbromide lost 0.1484 grm. Br.

B. " " " 0.1446 grm. Br.

Difference . . . . . 0.0038 grm. Br.

	Percentage of total side-chain bromine removed.	B in per cent of A.
A.	46.36	100.
B.	45.21	97.5
	<u>1.15</u>	<u>2.5</u>

From these results it appears that the method can be trusted within 0.0062 grm. of bromine, or 5.3 per cent when the largest number is taken as 100.\*

The results of the experiments, comparing the rate of decomposition of the three monobrombenzylbromides, are given in the following table; the first column of which gives the time from the addition of

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\* The results of these experiments cannot be compared with those given in Table I, because the quantity of alcohol used was not the same.

the acetate till the reaction was stopped by dilution with water, while in the other columns, under the name of each substance the amount of bromine removed is given, — first in grammes, and second in percentages of the total amount of side-chain bromine.

TABLE I.

Time in minutes.	Parabrombenzylbromide.		Metabrombenzylbromide.		Orthobrombenzylbromide.	
	Bromine in grammes.	Per cent of total.	Bromine in grammes.	Per cent of total.	Bromine in grammes.	Per cent of total.
5	0.0855	26.73	0.0621	19.41	0.0533	16.65
10	0.1261	39.41	0.0968	30.25	0.0700	21.88
20	0.1752	54.75	0.1329	41.54	0.1015	31.72
30	0.1880	58.76	0.1517	47.43	0.1412	44.13

On representing the percentages of the total side-chain bromine removed by curves, in which horizontal distance represents time, vertical per cents, it is found that those given by the para and meta compounds are comparatively regular, but that the ortho curve is decidedly irregular. The same fact is brought out by the following table, in which the amount of bromine removed from the ortho and meta compounds in each experiment is given in percentages of the amount derived from the para compound in the same experiment.

TABLE II.

Time in minutes.	Para.	Meta.	Ortho
5	100	73.	62.
10	100	77.	55.
20	100	76.	58.
30	100	81.	75.

The differences between the relative amounts of bromine removed from the meta compound in the first three experiments, tabulated above, fall within the limit of error of the process, which amounts to over five per cent when the numbers are given in this form; and, although the amount of bromine removed during thirty minutes is somewhat larger, the difference between this and the highest of the other numbers is only four per cent. It is probable, therefore, that the relative rate of decomposition for the para and meta compounds remains constant in the interval of time between five and thirty minutes; and that the slight increase in the numbers with the time in the experiments at 5, 20, and 30 minutes, is entirely accidental, although

this point can be settled only by a new series of observations with a more accurate method. If this is assumed to be true, the mean of the numbers given in the meta column will represent the rate at which the metabrombenzylbromide is attacked, in comparison with that for the para compound taken as 100. This mean is 77; that is, about three quarters as much bromine is removed from the meta as from the para compound in the same length of time.

The numbers given in the ortho column show much more serious deviations, the maximum difference amounting to twenty per cent; but, as I observed that these numbers increased essentially with the time during which the specimen had stood exposed to the air of a desiccator, the experiments having been tried in the following order, — 10 minutes, 55 %; 5 minutes, 64 %; 20 minutes, 58 %; 30 minutes, 75 %, — I was led to the conclusion that the substance was undergoing decomposition, which afterwards was proved to be the case by the following analyses: I. made before, II. and III. after, the series of experiments.

- I. 0.2375 grm. of orthobrombenzylbromide gave, by the method of Carius, 0.3565 grm. AgBr.
- II. 0.2950 grm. of substance gave 0.3705 grm. AgBr.
- III. 0.4100 grm. of substance gave 0.5210 grm. AgBr.

Calculated for $C_7H_5Br_2$ .		Found.		
		I.	II.	III.
Bromine	64.00	63.87	53.46	54.07 *

The complete study of this decomposition must be postponed till a future paper. I can only say here, that no appreciable amount of free hydrobromic acid could be detected in the substance analyzed above, and that I have often found crystals of orthobrombenzoic acid in specimens of orthobrombenzylbromide which had stood exposed to dry air for several months. Whatever may be the nature of the change, it is evident that the ortho numbers are of no value; and no attempt was made to correct them by new experiments, because such an unstable substance as the orthobrombenzylbromide is entirely unfit for work of this sort.

I will add a number of other comparisons, which were made by less accurate processes during the elaboration of the method. They are given as in Table II., the amount of bromine removed from the para

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\* As these experiments were made before the orthobrombenzylbromide was obtained in the solid state, I had no criterion of its purity except the analysis.

compound being taken as 100 in each experiment, and the amounts from the meta and ortho compounds given in percentages of this. Either two or four grammes of substance were taken in each experiment.

TABLE III.

Time in Minutes.	Para.	Meta.	Ortho.
22	100	78	54
22	100	73	52
23	100	78	54
21	100	—	48
Mean,	100	76	52

These numbers, entitled to very little consideration as independent experiments, confirm the preceding results from the meta compound, even more closely than could be expected when the large limit of error is remembered; and further would seem to indicate that the rate for the ortho compound is about one half that for the para, if it is assumed, as before, that the relative rate does not vary with the length of time during which the reaction has run; a result confirmed by the experiment made first in the preceding series, and therefore entitled to the most weight, which gave 55 %.

Berthelot and Pean de St. Gilles,\* in their classic researches on etherification, found that after a certain time the water set free in the reaction prevented further formation of the ether; in other words, that there was a limit to etherification. Although it did not seem probable that there would be such a limit to this reaction, some experiments were tried to test the question, with the following results:—

I. Time somewhat more than two hours:—

1 grm. of parabrombenzylbromide lost 0.3203 grm. of bromine.

1 grm. of metabrombenzylbromide lost 0.2701 grm. of bromine.

0.8200 grm. of parachlorbenzylbromide lost 0.3082 grm. of bromine.

To this may be added the following, in which the method was somewhat different; in II. common alcohol being used, and in III. the reaction taking place in a sealed tube, with dilute alcohol as the solvent.

II. Two portions of parabrombenzylbromide, 1 grm. each, lost in twenty-five minutes 0.3113 grm. and 0.3074 grm. of bromine.

III. In thirty minutes 0.3046 grm. and 0.3093 grm. of bromine.

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\* Ann. Chim. Phys., 3d ser., lxviii. p. 225.

The results of these three experiments, calculated into percentages of the side-chain bromine, are given for the sake of comparison in the following table:—

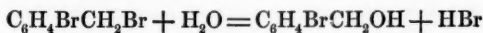
TABLE IV.

I.	II.	III.
Para. 100.1	Para. 97.3	Para. 95.3
Meta. 84.4	" 96.1	" 96.7
Chlor. 96.4		

Owing to the different conditions under which they were made these series of experiments are not comparable with each other, or with the series given in Tables I. and II., even I. not having been made under exactly the same conditions; they show, however, that there is no limit to the reaction in the case of the parabrombenzylbromide and probably none in the case of any of these substances.

*Action of Water on the Monobrombenzylbromides.*

Another entirely different method was also tried, which consisted in heating the substituted benzylbromides with water in sealed tubes, and determining the amount of hydrobromic acid formed by the reaction,—



For this purpose one gramme of each substance was weighed in a tube about 14 cm. long and 2 cm. wide; 5 c.c. of water were added, and, after sealing, the tubes were put into a hot chloride of calcium bath, provided with an air-tight tin cover carrying a return-cooler, which thus was kept at a constant temperature throughout the process. After a definite time the tubes were removed, cooled as rapidly as possible with cold water, and the contents washed into a beaker, and titrated with a standard solution of baric hydrate. The following experiments were made with two portions of parabrombenzylbromide to test the process.

Time in Hours.		Temperature.	Percentage of side-chain bromine removed.	
			Portion a.	Portion b.
I.	2	132°–134°	16.05	13.3
II.	2½	110°–134°	17.8	16.3
		I.	II.	
	a	100	100	
	b	83	92	

The marked want of agreement between these numbers is undoubtedly due to the fact that the mixture was not homogeneous, and therefore the differences in size of the surface of contact between the water and benzylbromide in the different tubes had a marked effect on the result [Compare p. 242].

In spite of the inaccuracy of the method two experiments were carried through with the following results:—

TABLE V.  
TEMPERATURE 135°.

Time in hours.	Parabrombenzylbromide.		Metabrombenzylbromide.		Orthobrombenzylbromide.	
	Bromine in grammes.	Per cent of total.	Bromine in grammes.	Per cent of total.	Bromine in grammes.	Per cent of total.
6	0.1421	48.85			0.0763	23.55
6	0.1268	39.15	0.0969	29.9	0.0918	28.35

These results calculated into the form of Table II. become:—

Para.	Meta.	Ortho.
100		54
100	76	72

The very high number for the ortho compound in the second experiment is probably due to a previous decomposition of the substance similar to that observed in the principal series of experiments [See page 247]. The other results, as far as they go, confirm those obtained by the acetate method.

In the following table all the numbers thus far obtained are compared:—

TABLE VI.  
ACETATE METHOD.

Time.	Para.	Meta.	Ortho
5'	100	72	64
10'	100	77	55
20'	100	76	58
30'	100	81	75
21'	100	—	48
22'	100	78	54
22'	100	73	52
23'	100	78	54

WATER METHOD.			
6 hours	100		54
6 hours	100	76	72
Mean	100	76	59

A series of comparative experiments with parachlorbenzylbromide, parabrombenzylbromide and paraiodbenzylbromide was also made by the sodic acetate method, which indicated that they lose bromine at the same rate, when they are used in molecular proportions. I will give here, however, only the results from the last series of experiments, as in the others I did not succeed in overcoming some of the sources of error mentioned in the introduction wholly to my satisfaction. These results are given as in Table II.

Time in Minutes.	Parachlorbenzylbromide.	Parabrombenzylbromide.	Paraiodbenzylbromide.
25	100	97	99

#### Summary.

The results of this investigation are, — 1. The side-chain bromine is removed from the three monobrombenzylbromides approximately at the following rates: —

Para.	Meta.	Ortho.
100	76	55 (?)
or 4	3	2 (?)

when the quantity removed is less than 60 per cent of the whole.

2. From parachlor-, parabrom-, and paraiodbenzylbromide at essentially the same rate, if quantities proportional to their molecular weights are used.

All these results need confirmation by more accurate experiments, but, as Menschutkin in one of the papers\* of his beautiful series on the rate of etherification (the first† of which was published a year after the appearance of a preliminary notice‡ of my work) has announced his intention of studying the effect of aromatic isomerism, and with his better chosen reaction and more delicate method will be able to do the work much more easily and accurately than I could, I have decided not to pursue the subject farther.

So far as I have been able to find, the only paper on this subject, as yet published, is one by Post and Mehrtens,§ who describe a single

\* Ann. Chem. Pharm., 197, p. 225.

‡ Ber. d. ch. G. 1876, p. 931.

† Ber. d. ch. G. 1877, p. 1728.

§ Ber. d. ch. G. 1875, p. 1549.

attempt to make out the relative acidity of the three nitrophenols by treating weighed amounts of baric carbonate with solutions of the corresponding quantity of the three isomeres, and after one week determining the amount of baric carbonate dissolved. In this way they got results which calculated in percentages of the amount from the para compound become:—

Para. m.pt. 115°.	Meta. m.pt. 96°.	Ortho. m.pt. 45°.
100	57	93

and, therefore, agree with mine neither in order nor ratio.

### ELEVENTH PAPER.

As the preceding paper has brought the first part of these researches to a conclusion, I have thought it best to give in the present paper certain corrections and additions which will leave this division of the subject in a more satisfactory state.

#### *Parabrombenzyl Compounds.*

In preparing the alcohol of this series during the work described in the preceding paper, I was surprised to find that its melting-point was much higher than that given by Mr. Lowery in the second paper\* of the series, and as in addition to this some portions of that work were left in a decidedly fragmentary state, I have thought it best to submit the parabrombenzyl compounds to a complete revision, which I have done with the following results:—

*Parabrombenzylalcohol*,  $C_6H_4BrCH_2OH$ . This was prepared from the acetate, and purified by crystallization from ligroin, which is by far the best solvent for all the derivatives of the substituted benzyl-bromides described in these papers.

0.2298 grm. of substance gave 0.3765 grm. of  $CO_2$  and 0.0789 grm. of  $H_2O$ .

	Calculated for $C_6H_4BrOH$ .	Found.
Carbon	44.92	44.69
Hydrogen	3.74	3.82

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\* These Proceedings, xii. (n. s. iv.) p. 221.



The melting-point of the pure alcohol was  $77^{\circ}$ .\* In other respects its properties are given correctly by Mr. Lowery.

*Parabrombenzyleyanide* melts at  $47^{\circ}$  ( $46^{\circ}$  Lowery). The *alpha-toluylic acid* as before at  $114^{\circ}$ .

*Parabrombenzylsulphocyanate*,  $C_6H_4BrCH_2SCN$ , melts at  $25^{\circ}$  as given by Mr. Lowery. As this melting-point is much lower than would be expected from that of the benzylsulphocyanate ( $36^{\circ}$ – $38^{\circ}$  Henry,  $41^{\circ}$  Barbaglia), I thought it advisable to confirm its formula by the following new analyses:—

0.2318 grm. of substance gave 0.2447 grm. of  $BaSO_4$ .

0.3804 grm. of substance gave 0.3125 grm. of  $AgBr$ .

	Calculated for $C_6H_4BrSCN$ .	Found.
Sulphur	14.03	14.50
Bromine	35.09	34.95

*Parabrombenzylamines*. Parabrombenzylbromide acts on alcoholic ammonia in the cold, giving a mixture of the three amines, or their bromides, from which the pure compounds can be easily obtained by washing out the bromide of the primary amine with water, treating the residue with sodic hydrate, and separating the secondary from the tertiary by crystallization from alcohol.

The *primary amine*, set free from its bromide with sodic hydrate, is an oil, which can be distilled with steam, and is soluble in ether; it is rapidly converted into the carbonate by exposure to the air.

The *carbonate*, obtained by treating the free base with carbonic dioxide, consists of little white prisms arranged in radiating groups, which melt at  $131^{\circ}$ – $133^{\circ}$ , are soluble in water and alcohol, insoluble or nearly so in ether, benzol, and carbonic disulphide.

The *chloride*, made from the carbonate with hydrochloric acid, forms flattened needles melting with apparent decomposition at  $260^{\circ}$ , soluble in water and hot alcohol, but slightly soluble in cold alcohol, and essentially insoluble in ether, benzol, and carbonic disulphide.

The *chlorplatinate*  $(C_6H_4BrCH_2NH_2)_2PtCl_6$  made from the chloride, and purified by washing with water, gave the following result on analysis:—

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\* The high melting-point of the parabrombenzylalcohol made me think that the paraiodbenzylalcohol might melt at a temperature higher than that given by Mr. Mabery in the third paper of this series. He has, however, at my request recrystallized some of it from ligroin, and found that the melting-point remained the same ( $72^{\circ}$ ) even after three crystallizations.

0.3020 grm. of the salt gave 0.0755 grm. of Pt.

Calculated for $(C_6H_4BrCH_2)_2PtCl_6$ .	Found.
Platinum 25.16	25.00

It crystallizes in orange-brown plates, apparently of the monoclinic system, grouped in forms like frost, and is but slightly soluble in cold water, more so in hot, and in alcohol.

The *secondary amine*  $(C_6H_4BrCH_2)_2NH$  is left on evaporating its alcoholic solution as an oil, which solidifies on stirring, and can be obtained crystallized. It melts at  $50^\circ$ , and is very freely soluble in alcohol and ether.

The *chloride* is obtained in glistening rhombic scales, often penately twinned, by adding strong hydrochloric acid to an alcoholic solution of the base; it melts at  $283^\circ$ , and is nearly insoluble in cold, somewhat more soluble in hot water, or alcohol, insoluble in ether.

The *chlorplatinate*  $[(C_6H_4BrCH_2)_2NH_2]_2PtCl_6$  formed by adding chlorplatonic acid to an alcoholic solution of the free base, after being washed with alcohol, and dried at  $100^\circ$ , gave the following result on analysis:—

0.4716 grm. of salt gave 0.0802 grm. of Pt.

Calculated for $[(C_6H_4Br)_2NH_2]_2PtCl_6$	Found.
Platinum 17.58	17.01

It is a yellow powder, nearly insoluble in alcohol and water.

The *tertiary amine*  $(C_6H_4BrCH_2)_3N$  was purified by recrystallization from ether, or from ligroin; in either case a matted mass of needles looking like cotton was obtained, but the melting-point differed according to the solvent used, the crystals from ligroin showing the constant melting-point  $92^\circ$ , those from common ether the constant melting-point  $76^\circ$ – $78^\circ$ . Two recrystallizations from ligroin were enough to raise the melting-point of the crystals from ether to  $92^\circ$ , while the same number from ether lowered it again to  $76^\circ$ – $78^\circ$ . The following analyses, however, prove that the substance dried *in vacuo* has the composition of the tertiary amine, whichever solvent was used in its purification.

- I. 0.3800 grm. of the crystals from ligroin, m.pt.  $92^\circ$ , gave 0.6680 grm.  $CO_2$  and 0.1200 grm.  $H_2O$ .
  - II. 0.2515 grm. of the crystals from ether gave 0.4430 grm.  $CO_2$  and 0.0890 grm.  $H_2O$ .
- 0.2020 grm. of the crystals from ether gave 0.2175 grm. AgBr.  
0.1888 grm. gave 0.2022 grm. AgBr.

	Calculated for (C <sub>7</sub> H <sub>6</sub> Br) <sub>3</sub> N.	I. (Ligroin.)	Found.	II. (Ether.)
Carbon	48.09	47.93		48.03
Hydrogen	3.44	3.51		3.93
Bromine	45.81		45.82	45.56

*Properties.* Fine white needles matted together into a woolly mass, or forming circular radiated groups, insoluble in water, very slightly soluble in alcohol hot or cold, not freely in warm ether, but easily in hot ligroin, from which it crystallizes on cooling. In the preparation from alcoholic ammonia and parabrombenzylbromide it sometimes appears in needles 12 cm. long.

No definite chloride could be obtained even by precipitating the platinum as sulphide from the chlorplatinate, and washing with alcohol, as this gave only a viscous varnish.

*Triparabrombenzylamine Chlorplatinate* [(C<sub>6</sub>H<sub>4</sub>BrCH<sub>2</sub>)<sub>3</sub>NH]<sub>3</sub>PtCl<sub>6</sub>, made by adding chlorplatinic acid to an ethereal solution of the free base, and purified by washing with water, alcohol, ether, and ligroin, gave the following result on analysis:—

0.3254 grm. of the salt gave 0.0432 grm. of Pt.

	Calculated for [(C <sub>6</sub> H <sub>4</sub> Br) <sub>3</sub> NH] <sub>3</sub> PtCl <sub>6</sub> .	Found.
Platinum	13.51	13.28

Corn-yellow indistinct crystals, insoluble or nearly so in all the common solvents.

*Monoparaiodbenzylamine, C<sub>6</sub>H<sub>4</sub>ICH<sub>2</sub>NH<sub>2</sub>.*

Mr. C. F. Mabery has, at my request, prepared this substance, which he had not obtained in quantity sufficient for analysis, when he published his paper on the paraiodbenzyl compounds, by heating paraiodbenzylbromide with a large excess of alcoholic ammonia in a sealed tube to 120°. It is easily separated from the secondary and tertiary amines by washing with water, and, upon adding sodic hydrate to the solution of its bromide thus obtained, and extracting with ether, the carbonate is left as the ether evaporates in the form of a white solid melting at 113°.

The *chloride* made from the carbonate with hydrochloric acid forms slender white needles melting at 240°, readily soluble in water and alcohol, sparingly in ether.

The *chlorplatinate* (C<sub>6</sub>H<sub>4</sub>ICH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>PtCl<sub>6</sub> made by adding chlor-

platinic acid to the chloride, and purified by washing with alcohol, gave the following result on analysis:—

0.3560 grm. of the salt gave 0.0795 grm. Pt.

Calculated for $(C_7H_5INH_2)_2PtCl_6$ .		Found.
Platinum	22.47	22.34

### *Metabrombenzyl Compounds.*

In the study of these substances which I undertook with Mr. J. Fleming White, so many difficulties were encountered that the work was far from done at the end of the last college year. As, however, Mr. White has left Cambridge, and I see no immediate prospect of returning to this subject, I have decided to publish our results on the alcohol, and the melting-point of the alphetoluylic acid, reserving an account of the amines until our, at present contradictory, results have been submitted to a thorough revision.

*Metabrombenzylalcohol*,  $C_6H_4BrCH_2OH$ , was made directly from metabrombenzylbromide by heating it with water in a sealed tube to  $130^\circ$  for 24 hours, or from the acetate, obtained by heating the bromide with an alcoholic solution of sodic acetate, by decomposing it with aqueous ammonia in a sealed tube at  $150^\circ$ , or with an aqueous solution of sodic hydrate in a flask with a return-cooler. The oil thus obtained was purified by distillation with steam, dried *in vacuo* and analyzed.

0.2890 grm. of substance gave according to Carius 0.2913 grm. AgBr. 0.4660 grm. gave 0.4690 grm. AgBr.

Calculated for $C_7H_5BrOH$ .		Found.	
Bromine	42.79	42.88	42.84

The substance is a colorless oil heavier than water, which did not solidify in a freezing mixture even when vigorously stirred with a sharp rod.

The *cyanide*, as obtained by the action of an alcoholic solution of potassic cyanide on metabrombenzylbromide, is a dark-colored oil, and is converted by heating with strong hydrochloric acid in a sealed tube to  $115^\circ$  into the *metabromalphetoluylic acid*, melting-point  $97^\circ$ , which resembles the isomeric acids already described very closely. The complete study of this acid must be postponed for the present.

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### XIII.

#### VARIABLE STARS OF SHORT PERIOD.

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Presented February 9, 1881.

IN a recent communication to this Academy \* the following classification of the variable stars was proposed: —

I. Temporary stars. Examples, Tycho Brahe's star of 1572, new star in Corona, 1866.

II. Stars undergoing great variations in light in periods of several months or years. Examples,  $\alpha$  *Ceti* and  $\chi$  *Cygni*.

III. Stars undergoing slight changes according to laws as yet unknown. Examples,  $\alpha$  *Orionis* and  $\alpha$  *Cassiopeiæ*.

IV. Stars whose light is continually varying, but the changes are repeated with great regularity in a period not exceeding a few days. Examples,  $\beta$  *Lyræ* and  $\delta$  *Cephei*.

V. Stars which every few days undergo for a few hours a remarkable diminution in light, this phenomenon recurring with great regularity. Examples,  $\beta$  *Persei* and *S Cancri*.

A discussion was given, in the article referred to, of the stars of the last class. It was shown that in the case of  $\beta$  *Persei* at least, the observed variations could be very satisfactorily explained by the theory that the reduction in light was caused by a dark eclipsing satellite. The dimensions of this satellite and of its orbit were then computed. The variations of the stars of the fourth class will be considered in the present paper. Both of these papers must be regarded as preliminary, rather than final, discussions. Observations are now in progress at the Harvard College Observatory which greatly increase the precision of our knowledge of many of the constants involved. When these are completed, a revision of the whole investigation is much to be desired. To avoid all prejudice, the present papers are made to

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\* Proc. Amer. Acad., xvi. 1.

depend entirely on the work of previous observers. Approximate methods are depended upon throughout, where a rigorous computation would have been employed, if the results were to be regarded as final. In Table I. is given a list of all the known variable stars whose periods are less than three months. The successive columns give a current number, the number in Schönfeld's Second Catalogue,\* the name of the star, and the class to which it belongs, when this is known with certainty. Then follow the right ascension and declination for 1880, the period in days, and the magnitudes at maximum and minimum. The data for the southern stars which are not given by Schönfeld are taken from the Uranometria Argentina. The last columns give the name of the discoverer and the year in which the variability was detected.

TABLE I.—VARIABLE STARS OF SHORT PERIODS.

Number.	Schön.	Name.	Cl.	R. A. 1880.	Dec. 1880.	Period.	Max.	Min.	Discoverer.	Year.
				<i>h. m.</i>	<i>° ′</i>					
1 ..	—	Cephei	V	0 51.7	+81 14	2.49	7	10	Ceraski	1880
2 17	$\beta$	Persei	V	3 0.4	+40 30	2.87	2.2	3.7	Montanari	1669
3 19	$\lambda$	Tauri	V	3 54.0	+12 9	3.95	3.4	4.2	Baxendell	1848
4 32	<i>T</i>	Monocerotis	IV	6 18.7	+ 7 9	27.00	6.2	7.6	Gould	1871
5 34	<i>S</i>	Monocerotis	..	6 34.4	+10 0	3.40	4.9	5.4	Winnecke	1867
6 36	$\zeta$	Geminorum	IV	6 57.0	+20 45	10.16	3.7	4.5	Schmidt	1844
7 ..	<i>U</i>	Monocerotis	..	7 25.1	+ 9 32	46.00	6.0	7.2	Gould	1873
8 47	<i>S</i>	Canceri	V	8 37.1	+19 28	9.48	8.2	9.8	Hind	1848
9 ..	<i>N</i>	Velorum	..	9 27.6	+56 30	4.25	3.4	4.4	Gould	1871
10 ..	<i>I</i>	Carinae	..	9 42.0	+61 57	31.25	3.7	5.2	Gould	1871
11 ..	<i>R</i>	Muscae	..	12 34.8	+68 45	0.89	6.6	7.4	Gould	1871
12 66	<i>W</i>	Virginis	..	13 19.8	+ 2 45	17.27	8.7-9.2	9.8-10.4	Schönfeld	1866
13 74	$\delta$	Librae	V	14 54.6	+ 8 2	2.32	4.9	6.1	Schmidt	1859
14 ..	<i>T</i>	Triang. Aust.	..	14 58.6	+68 15	1.00	7.0	7.4	Gould	1871
15 ..	<i>R</i>	Triang. Aust.	..	15 9.1	+66 3	3.40	6.6	7.5	Gould	1871
16 75	<i>U</i>	Coronae	V	15 13.3	+32 5	3.45	7.6	8.8	Winnecke	1869
17 96	$\eta$	Herculis	..	17 12.9	+33 14	38.50	4.6	5.4	Schmidt	1869
18 98	<i>X</i>	Sagittarii	..	17 40.0	+27 47	7.01	4	6	Schmidt	1866
19 99	<i>W</i>	Sagittarii	..	17 57.4	+29 35	7.59	5	6.5	Schmidt	1866
20 ..	—	Sagittarii	..	18 9.8	+34 9	2.42	6.2	7.4	Gould	1871
21 103	<i>U</i>	Sagittarii	..	18 24.8	+19 13	6.75	7.0	8.3	Schmidt	1866
22 105	<i>R</i>	Senti	..	18 41.1	+ 5 50	71.10	4.7-5.7	6.0-8.5	Pigott	1795
23 ..	$\kappa$	Pavonis	..	18 44.6	+67 23	9.10	4.0	5.5	Gould	1872
24 106	$\beta$	Lyræ	IV	18 45.6	+33 13	12.91	3.4	4.5	Goodricke	1784
25 107	$\beta$	Lyræ	..	18 51.7	+43 47	46.00	4.3	4.6	Baxendell	1856
26 108	<i>S</i>	Coron. Aust.	..	18 53.1	+37 7	6.20	9.8	11.5?	Schmidt	1866
27 109	<i>R</i>	Coron. Aust.	..	18 53.8	+37 7	54.00	10.6-11.5	<12.5	Schmidt	1866
28 116	<i>S</i>	Vulpeculae	..	19 43.5	+26 59	67.50	8.4-8.9	9.0-9.5	Rogerson	1837
29 118	$\eta$	Aquilæ	IV	19 46.4	+ 0 42	7.18	3.5	4.7	Pigott	1784
30 122	<i>R</i>	Sagittæ	..	20 8.6	+15 22	70.42	8.5-8.7	9.8-10.4	Baxendell	1859
31 137	$\delta$	Cephei	IV	22 24.7	+57 48	5.37	3.7	4.9	Goodricke	1784

\* Zweiter Catalog von veränderlichen Sternen. Mannheim, 1875.

From this table it appears that only six stars of the fifth class are as yet known. Although the published observations of some of the others are insufficient to determine the nature of their variations, it is probable that most of them belong to the fourth class. The first star on the list, which is DM. 81°.25, has been designated as *T Cephei*,\* but the use of this name has created much confusion. In 1863,† Arge-lander announced the variability of the star DM. 55°.2943, and this star is called *T Cephei* in Chambers' Astronomy, p. 586. In 1879, Ceraski‡ announced that DM. 67°.1291 was variable. When correcting its position § he called it *T Cephei*. This correction is quoted in the "Astronomical Register," xviii. 322, under the heading "W. Ceraski's new Variable," apparently confounding it with Ceraski's last discovery, DM. 81°.25.

The most natural explanation of the variation of a star of short period is that it is due to its rotation around its axis.

In the Annals of the Harvard College Observatory, xi. 264, the variation in light of Iapetus, the outer satellite of Saturn, is discussed on this hypothesis. It is there shown that if the axis of revolution is perpendicular to the line of sight, the variation of light,  $L$ , may be approximately represented by the formula,  $L = a + b \sin v + c \cos v + d \sin 2v + e \cos 2v$ ;  $a$  here denotes the mean light,  $v$  the angle of rotation,  $b$  and  $c$  are constants depending on the comparative brilliancy of the two hemispheres, each of which is supposed to be of uniform intensity, but one brighter than the other;  $d$  and  $e$  depend on a supposed deviation of the body from the form of a solid of revolution. This equation may also be written in the form  $L = a + m \sin (v + \alpha) + n \sin (2v + \beta)$ , in which  $\alpha$  depends upon the angular position of the plane separating the two hemispheres from the line of sight at the epoch from which the variation in light is reckoned;  $\beta$  in like manner depends upon the positions in which the body subtends its largest and smallest discs. Our problem then is to see how far this equation will represent the variation in light of all the stars of the fourth class.

Both of these proposed causes of variation may be criticised as improbable; but what could be more improbable than the phenomenon itself, were it not verified by observation? With our present knowl-

\* Science Observer, iii. 30, 38, 48. English Mechanic and World of Science, xxxii. 297. Astron. Nach. xcix. 87.

† Astron. Nach., lxi. 281.

‡ Astron. Nach., xciv. 175.

§ Astron. Nach., xcvi. 239.



edge of the constitution of the stars it would seem extremely unlikely that certain of them would lose half their light at regular intervals of from one to twelve days. If it can be shown that the hypothesis satisfies the observed facts, it seems unreasonable to deny it until some more probable explanation can be offered. The difference in brightness of the two sides of a star may be due to spots like those of our sun, to large dark patches, or to a difference in temperature. In the latter case, observations of the distribution in light in the spectrum at the maxima and minima might show a greater variation in the blue than in the red portions. If the body had the form of an oblate ellipsoid rotating around one of its longer axes, its condition of equilibrium would be unstable. If, however, it was a prolate ellipsoid it would be in stable equilibrium, and if sufficiently rigid might revolve in this way indefinitely. If, like our sun, it was in a fluid condition, we might anticipate a return to the form of a solid of revolution. Jacobi has however shown\* that a fluid ellipsoid having three unequal axes may be in equilibrium when revolving around its shortest axis. An analogous case is found in Plateau's experiment, where a globule of oil suspended in alcohol and water is made to revolve. With a sufficient velocity the globule, if slightly eccentric, elongates before throwing off a satellite. We may also assume the existence of two nuclei, or that the two components of a binary star are so close together that both are enveloped in the incandescent gas or photosphere.

Another equation of condition would thus be furnished which might serve to determine the absolute diameter of the star in miles. Thus the observations discussed below give the relative dimensions of two of the axes, and the condition that the body shall be in equilibrium will determine the relative length of the axis of revolution. If the star was an ellipsoid of revolution we could compute the flattening at the poles from the diameter and the time of revolution; we could also compute the diameter if the other two constants were given. Although the problem is more complex, evidently the same principle may be applied to an ellipsoid with three unequal axes.

Four of these stars,  $\zeta$  *Geminorum*,  $\beta$  *Lyræ*,  $\eta$  *Aquilæ*, and  $\delta$  *Cephei*, have been observed with great care, so that their variations are known with much precision. Each will therefore be discussed in turn, according to the following method. As the variation is periodic, it will be convenient to denote the time by an angle,  $v$ , such that  $360^\circ$  shall correspond to one period or revolution of the star. We now wish the light

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\* Poggendorff's *Annalen*, xxxiii 229; see also *Journ. Frank. Inst.* cx. 217.



corresponding to  $v = 0^\circ, 15^\circ, 30^\circ, 45^\circ$ , etc. The period is divided into twenty-four equal parts, and the number of grades corresponding to each is taken from the light curves. Argelander and Schönfeld give the number of grades for each hour, and the number of grades was found from their tables by interpolation. Oudemans represents his results graphically, and the grades were taken from his curves by inspection. These curves were used rather than the original observations, in order to reduce the accidental errors. The results are free from prejudice, since they were drawn by the observers themselves without regard to any theory. They are, however, open to the objection that small systematic errors may be present which are not easily detected.

We must next pass from grades to the actual intensities of light. For this purpose we cannot rely on an assumed value of a grade, since we have no certainty that this will be the same for lights of different intensity. Accordingly, the comparison stars used by each observer are compared with the measures of Wolff.\* Points were constructed whose abscissæ equal the assumed light of each comparison star in grades, and their ordinates, the logarithms of the light as measured by Wolff. A smooth curve was then drawn through these points, and served to convert the grades into logarithms. The readings are only made to hundredths, since one unit in this place corresponds to one-fortieth of a magnitude, and all the curves are uncertain by much more than this amount. The largest logarithm is then subtracted from all the others, and the number corresponding to the difference gives the intensity of the light. This is multiplied by one hundred, so that the results are given in percentages.

In the equation,  $L = a + m \sin (v + \alpha) + n \sin (2v + \beta)$ ,  $a$  is found from the mean of all the observed values of  $L$ . The other constants might be found from a solution by least squares, forming twenty-four equations of condition with the twenty-four deduced values of  $L$ . Sufficient accuracy is, however, obtained by approximate graphical methods. By adding together the values of  $L$ , corresponding to values of  $v$  differing  $180^\circ$ , we eliminate the term  $m \sin (v + \alpha)$ . Their differences, in like manner, eliminate  $n \sin (2v + \beta)$ . Each then may thus be found independently of the others.

§ *Geminorum*. In 1848, Argelander gave a light curve of this star.†

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\* Photometrische Beobachtungen an Fixsternen, Leipzig, 1877.

† Astron. Nach., xxviii. 33.

Table II. gives the data for converting the grades into light ratios by means of the comparison stars. The successive columns give the name of the star, its light in logarithms as measured by Wolff, its light in grades assumed by Argelander, the corresponding ordinate of the curve, and the second column minus the fourth, or the assumed errors.

TABLE II.—COMPARISON STARS FOR  $\zeta$  GEMINORUM.

Name.	Wolff.	Grades.	Curve.	$W - C$
$\xi$ Geminorum . . . .	8.81	9.9	8.81	.00
$\delta$ Geminorum . . . .	8.73	8.8	8.74	— .01
$\lambda$ Geminorum . . . .	8.68	8.0	8.70	— .02
$\iota$ Geminorum . . . .	8.66	6.0	8.64	+ .02
$\nu$ Geminorum . . . .	8.58	3.3	8.58	.00
$\nu$ Geminorum . . . .	8.55	2.0	8.55	.00

The curve here agrees very well with the measurements, but its inclination is much greater for the brighter than for the fainter stars. In other words, a grade represents a much larger difference in magnitude when the star is bright than when faint. The change is, however, slight between the limits within which the curve is used.

Table III. gives a comparison of the light curve with theory. The successive columns give the angle  $v$ , the corresponding time from the minimum, and the observed light in grades, in logarithms, and in percentages. The next column gives the light computed by the formula,  $L = 89.6 + 10.0 \sin v$ ; this is followed by the residuals found by subtracting the computed from the observed brightness. As they show a perceptible systematic error, two more columns are given corresponding to the formula  $L = 89.6 + 10.2 \sin (v - 11^\circ.3)$ . This gives an entirely satisfactory agreement with observation, the average deviation amounting to less than one per cent. It cannot be reduced directly to magnitudes, since, when the light equals 100, one per cent equals .011 magnitudes, when 80, .014 magnitudes, and when 50, .022 magnitudes. The average deviation is accordingly only about one hundredth of a magnitude. Since two smooth curves are compared, the small irregular variations in the residuals are principally due to the neglected thousandths in the logarithm of the light. They are, however, probably far less than the real errors of the curves. The mean of the residuals is given in the last line of the table.

TABLE III.—VARIATION IN LIGHT OF  $\zeta$  GEMINORUM.

$v$ .	Time.		Gr.	Log.	Obs.	Comp.	$O - C$	Comp.	$O - C$
	$d$ .	$h$ .							
0	0	0.0	3.4	8.58	79	80	-1	79	0
15	0	10.2	3.6	8.58	79	80	-1	80	-1
30	0	20.3	4.1	8.59	81	81	0	82	-1
45	1	6.5	4.7	8.61	85	82	+3	84	+1
60	1	16.6	5.2	8.62	87	85	+2	86	+1
75	2	2.8	5.7	8.63	89	87	+2	89	0
90	2	12.9	6.1	8.64	91	90	+1	92	-1
105	2	23.0	6.5	8.65	93	92	+1	94	-1
120	3	9.2	6.9	8.66	96	95	+1	96	0
135	3	19.4	7.2	8.67	98	97	+1	98	0
150	4	5.5	7.3	8.67	98	98	0	100	-2
165	4	15.7	7.4	8.68	100	99	+1	100	0
180	5	1.8	7.4	8.68	100	100	0	100	0
195	5	12.0	7.3	8.67	98	99	-1	99	-1
210	5	22.2	7.1	8.67	98	98	0	98	0
225	6	8.3	6.8	8.66	96	97	-1	96	0
240	6	18.5	6.4	8.65	93	95	-2	93	0
255	7	4.6	6.0	8.64	91	92	-1	90	+1
270	7	14.8	5.5	8.63	89	90	-1	88	+1
285	8	0.9	5.0	8.61	85	87	-2	85	0
300	8	11.1	4.5	8.60	83	85	-2	83	0
315	8	21.3	4.0	8.59	81	82	-1	81	0
330	9	7.4	3.7	8.59	81	81	0	80	+1
345	9	17.5	3.5	8.58	79	80	-1	79	0
Mean . .							$\pm 1.1$	..	$\pm 0.5$

There seems to be no evidence of the term  $n \sin (2v + \beta)$ ; in other words, the star appears to be a surface of revolution, one side being about four-fifths of the brightness of the other. It is also possible that the star may be elongated with axes in the ratio of four to five, but of equal brightness on all sides, and that its time of revolution is 20.32 days, or double the period commonly given. In this case there may be a slight difference in brightness at the alternate maxima or minima which has hitherto escaped detection, because not anticipated. From the second formula we may infer that the true maximum and minimum precede that adopted by Argelander, by the angular amount of  $11.3^\circ$ , or 7.6 hours. As this would only affect the light curve by about a fiftieth of a magnitude, it might readily escape detection. It will be noticed that in this case the interval from maximum to minimum is equal to that from minimum to maximum, instead of, as is generally the case, exceeding it. A more direct determination of the correction to the minimum may be found from the light curve, by comparing the times at which the light is equal.

In Table IV. are given the light in grades, the corresponding times

taken from the light curves, and the time of the minimum, assuming that it lies midway between them. This last column is found by adding to the second column  $10^d 3.7^h$ , or the period of the star; adding to this the third column, and dividing the result by two; finally subtracting the quotient from the period,  $10^d 3.7^h$ . The mean of this value, or 7.4, agrees closely with that given above.

TABLE IV. — MINIMUM OF  $\zeta$  GEMINORUM.

Gr.	Increasing.		Decreasing.		Mean.
	d.	h.	d.	h.	
4.0	0	18.5	8	22.0	—5.6
5.0	1	12.0	8	0.5	—7.6
6.0	2	9.5	7	4.5	—6.9
7.0	3	13.5	6	2.0	—9.6

$\beta$  *Lyræ*. Light curves of this star were given by Argelander in 1842, *Astron. Nach.*, xix. 397, and in 1844, *De stella  $\beta$  Lyræ variabili disquisitio*. In 1859 he gave a more complete discussion of the problem.\* He divided his previous observations into three periods, and derived a curve from each; concluding that they differed from each other only by their accidental errors, he gave a curve representing the entire series.

Oudemans † gives a light curve from his observations, reduced to the same system as that given in Argelander's second publication. This differs so little from the last system of Argelander that the same curve, for reduction to logarithms, has been used for both. In no case, within the limits used, would the difference of the logarithms exceed one or two hundredths.

In 1870, Schönfeld gave another curve, *Astron. Nach.*, lxxv. 1. His grades represent a smaller variation in the light than Argelander's, and, like the latter, a grade is larger for the brighter stars than for the fainter, as in the case of  $\zeta$  *Geminorum*. The relation of the grades to the logarithms of the light is shown in Table V. The columns have the same meaning as in Table II., except that three additional columns are given for the comparisons of Schönfeld.

\* *De stella  $\beta$  Lyræ variabili commentatio altera*.

† *Zweijährige Beobachtungen der meisten jetzt bekannten veränderlichen Sterne*. Verhand. Akad. Amsterdam, 1856.

TABLE V.—COMPARISON STARS FOR  $\beta$  LYRÆ.

Name.	Wolff.	Argelander.			Schönfeld.		
		Grades.	Curve.	W — C	Grades.	Curve.	W — C
$\gamma$ Lyræ . .	8.89	12.7	8.87	+ .02	15.0	8.88	+ .01
$\mu$ Herculis . .	8.79	..	..	..	13.0	8.80	— .01
$\xi$ Herculis . .	8.70	10.3	8.75	— .05	10.3	8.71	— .01
$\sigma$ Herculis . .	8.69	7.6	8.69	.00	7.8	8.65	+ .04
$\epsilon$ Lyræ . .	[8.77]	4.9	8.60	[+ .17]	4.2	8.58	[+ .19]
$\zeta$ Lyræ . .	8.56	3.4	8.56	.00	2.9	8.56	.00
$\kappa$ Lyræ . .	8.56	2.6	8.55	+ .01	1.6	8.55	+ .01

The estimate of  $\epsilon$  Lyræ has not been included in drawing these curves. As the observations were made with the naked eye, in some cases aided by an opera-glass,  $\epsilon$  and  $\delta$  Lyræ were treated as a single star. Wolff gives the logarithms of their light as 8.50 and 8.45. Their combined light would therefore equal 8.77, or nearly half a magnitude brighter than would be inferred from the estimate in grades, using the curves derived from the other stars. This may also be expressed by the statement that, together, they appear only a quarter of a magnitude brighter than either would alone, while a star of their combined brightness should appear about three quarters of a magnitude brighter than the separate components. It is possible that their proximity affected their measures by Wolff, but this seems less probable since they would be readily separated by the telescope of a Zöllner photometer. Evidently,  $\epsilon$  Lyræ should not be used hereafter as a comparison star for this variable.

Table VI., like Table III., serves to compare the observations with theory. The first column gives the angle; the second, the corresponding time. Three sets of three columns each give the light in grades, in logarithms, and in percentages, for Argelander, Oudemans, and Schönfeld. Although the observations are not of equal value, it would be difficult to decide what weight should be given to each, and especially, to decide how large are the systematic errors to which each is subject. This last quantity should determine the weight, since the accidental errors are in a great measure eliminated by the smoothness of the light curves. Their mean, which is given in the next column, will accordingly be employed. The excess of the curve of each observer over the mean is given in the next three columns. An examination of the mean curve shows that it has two equal maxima symmetrically situated on each side of the point where  $v = 180^\circ$ . The curve must therefore have the form  $L = a + m \sin (v - 90^\circ) + n \sin (2v - 90^\circ)$ .

The mean value of  $L$  or  $a$  is 81.1. When  $v = 0^\circ$ ,  $L = a - m - n$ ; when  $v = 180^\circ$ ,  $L = a + m - n$ ;  $v = 90^\circ$  or  $270^\circ$ , gives  $L = a + m - n$ . Were there no accidental errors, either two of these three equations would determine  $m$  and  $n$ . After various trials the equation  $L = 81.1 + 4.1 \sin (v - 90^\circ) + 20.0 \sin (2v - 90^\circ)$  was found to give the most satisfactory results. The brightness computed by this formula, and the residuals found by subtracting them from the mean of the observed values, are given in the last two columns.

TABLE VI. — VARIATION IN LIGHT OF  $\beta$  LYRÆ.

v.	Time.	Argelander.			Oudemans.			Schönfeld.			Mean.	A - M	O - M	S - M	Comp.	O - C
		Gr.	Log.	Obs.	Gr.	Log.	Obs.	Gr.	Log.	Obs.						
0	d. h.															
15	0 0.0	3.4	8.56	49	4.0	8.57	49	3.6	8.57	51	50	-1	-1	+1	57	-7
30	0 12.9	5.0	8.60	56	5.0	8.60	56	5.2	8.58	58	55	+1	-3	-3	60	-5
45	1 1.8	9.2	8.71	72	8.0	8.67	62	9.2	8.71	71	68	+4	-6	-3	68	0
60	1 14.7	11.1	8.78	85	10.6	8.76	76	11.3	8.79	85	82	+3	-6	-3	78	+4
75	2 3.6	11.8	8.82	93	11.8	8.82	87	12.2	8.84	96	92	+1	-5	-4	89	+3
90	2 16.6	12.2	8.84	98	12.5	8.85	96	12.6	8.87	102	99	-1	-3	-3	97	+2
105	3 5.5	12.3	8.85	100	12.6	8.87	98	12.7	8.87	102	100	0	-2	-2	101	-1
120	3 18.4	12.1	8.84	98	12.4	8.85	93	12.5	8.86	100	97	+1	-4	-3	100	-3
135	4 7.3	11.8	8.82	93	11.7	8.81	85	11.9	8.82	91	90	-3	-5	-1	93	-3
150	4 20.2	11.2	8.79	87	10.7	8.76	76	10.9	8.77	81	81	-6	-5	0	84	-3
165	5 9.1	10.3	8.75	79	10.0	8.73	71	9.9	8.73	74	75	+4	-4	-1	75	0
180	5 22.0	8.8	8.69	69	9.2	8.71	68	9.1	8.70	69	69	0	-1	0	68	+1
195	6 10.9	8.6	8.69	69	9.1	8.70	66	8.9	8.70	69	68	+1	-2	+1	65	-3
210	6 23.8	9.4	8.71	72	9.5	8.72	69	9.3	8.71	71	71	+1	-2	0	68	-3
225	7 12.7	10.8	8.77	83	10.7	8.76	76	10.2	8.74	76	78	+5	-2	-2	75	-3
240	8 1.6	11.6	8.81	91	11.8	8.82	87	11.2	8.79	85	88	+3	-1	-3	84	+4
255	8 14.5	12.1	8.83	96	12.4	8.85	93	12.0	8.88	93	94	-2	-1	-1	93	+1
270	9 3.5	12.3	8.85	100	12.8	8.88	100	12.4	8.85	98	99	+1	+1	-1	100	-1
285	9 16.4	12.4	8.85	100	12.9	8.88	109	12.4	8.85	98	99	+1	+1	-1	101	-2
300	10 5.3	12.2	8.84	98	12.8	8.88	109	12.3	8.85	95	99	-1	+1	-1	97	+2
315	10 18.2	11.7	8.81	91	12.4	8.85	93	11.9	8.82	91	92	-1	+1	-1	89	-3
330	11 7.1	10.9	8.77	83	11.4	8.80	83	10.8	8.77	81	82	-1	+1	-1	78	+4
345	11 20.0	8.4	8.68	68	9.0	8.70	67	8.0	8.67	65	66	+2	0	-1	68	-2
Mean	12 8.9	4.0	8.58	54	4.7	8.59	51	4.2	8.58	53	53	+1	-2	0	60	-7
Mean . .											±1.9 ±2.5		±1.5		.. ±2.8	

These residuals are much larger than in the case of  $\zeta$  *Geminorum*; but this is to be expected, since the variations in light are greater. Evidently, if the changes were small, any two smooth curves would agree closely. Their average value amounts to about .04 of a magnitude, and their greatest value does not exceed the greatest difference of each of the observed curves from the others. The greatest errors of observation are those of the light of the comparison stars. The residuals near the principal minimum may be greatly reduced if the fainter comparison stars are assumed too faint, with a corresponding change in the value of the fainter grades. The rejection of  $\epsilon$  *Lyræ* in Table V., while its effect on Table VI. cannot be eliminated, may account for this apparent error. An increase in the logarithm of the

light by about .01 for grades 11 to 12 would reduce the residuals corresponding to  $v = 45^\circ, 60^\circ, 210^\circ, 225^\circ, 300^\circ$ , and  $315^\circ$ . The residuals for  $v = 120^\circ$  and  $135^\circ$  would, however, be increased. These changes are not to be recommended unless indicated by future photometric measures of the comparison stars.

$\eta$  *Aquilæ*. Argelander gave a light curve of this star in 1842, *Astron. Nach.*, xix. 399, based upon 174 observations taken by himself and by Heis. In 1857, he gave a second curve dependent on 411 of his own observations, *Astron. Nach.*, xlv. 97. In Table VII. the light of the comparison stars are given in grades and in logarithms, according to Wolff. The columns have the same meaning as in Table V. As  $\nu$  *Aquilæ* was not observed by M. Wolff, it is unavoidably excluded from the comparison.

TABLE VII. — COMPARISON STARS FOR  $\eta$  AQUILÆ.

Name.	Wolff	Grades.	Curve.	W—C	Grades.	Curve.	W—C
$\delta$ Aquilæ . .	8.85	13.3	8.85	.00	12.9	8.86	+.01
$\beta$ Aquilæ . .	8.74	8.0	8.72	+.02	8.1	8.71	— .03
$\epsilon$ Aquilæ . .	8.63	6.0	8.66	— .03	6.1	8.64	+.01
$\iota$ Aquilæ . .	8.57	3.0	8.57	.00	3.0	8.55	+.02
$\mu$ Aquilæ . .	8.43	—1.4	8.43	.00	—0.6	8.44	— .01
$\nu$ Aquilæ . .	...	—2.4	...	..	—1.8	...	..

The first seven columns of Table VIII. have the same meaning as in Table III. and give the values of  $v$ , of the time, of the light in grades, in logarithms, and in percentages, a computed value, and the residuals from this, or the fifth column minus the sixth. The computation is effected by the formula,  $L = 73.6 + 20.0 \sin (v - 60^\circ) + 6.0 \sin (2v - 120^\circ)$ . The last four columns give the light in grades, logarithms, and percentages, and the residuals according to the second curve of Argelander. The same theoretical formula is used in this case, adding 1 so that the positive and negative residuals shall be nearly equal. The light in this case,  $L' = L + 1 = 74.6 + 20.0 \sin (v - 60^\circ) + 6.0 \sin (2v - 120^\circ)$ .

$\delta$  *Cephei*. Argelander has given a light curve of this star in the *Astron. Nach.*, xix. 395. Curves are also given by Oudemans in the paper cited above, and by Schönfeld in *Astron. Nach.*, lxxv. 14. The relation of grades to logarithms is given in Table IX., for Argelander and Schönfeld. Oudemans has already reduced his scale to that of Argelander. Unfortunately, Wolff only measured those of the five



TABLE VIII.—VARIATION IN LIGHT OF  $\eta$  AQUILÆ.

<i>v.</i>	Time.		Gr.	Log.	Obs.	Comp.	<i>O</i> — <i>C</i>	Gr.	Log.	Obs.	<i>O</i> — <i>C</i>
0	<i>d.</i>	<i>h.</i>									
0	0	0.0	1.2	8.51	50	51	—1	2.1	8.52	54	+2
15	0	7.2	1.7	8.53	52	54	—2	2.4	8.53	55	0
30	0	14.4	3.2	8.57	58	58	0	3.5	8.56	59	0
45	0	21.5	4.8	8.63	66	65	+1	4.8	8.60	65	—1
60	1	4.7	6.3	8.67	72	74	—2	6.2	8.65	72	—3
75	1	11.9	8.1	8.72	81	82	—1	7.8	8.70	81	—2
90	1	19.1	9.6	8.76	89	89	0	9.5	8.75	91	+1
105	2	2.3	10.9	8.79	96	94	+2	10.6	8.78	98	+3
120	2	9.4	11.4	8.81	100	96	+4	10.9	8.79	100	+3
135	2	16.6	10.9	8.79	96	96	0	10.5	8.78	98	+1
150	2	23.8	10.1	8.77	91	94	—3	9.8	8.76	93	—2
165	3	7.0	9.2	8.75	87	90	—3	9.0	8.74	89	—2
180	3	14.2	8.5	8.74	85	86	—1	8.2	8.71	83	—4
195	3	21.3	8.0	8.72	81	82	—1	8.0	8.70	81	—2
210	4	4.5	7.6	8.71	79	78	+1	7.8	8.70	81	+2
225	4	11.7	7.2	8.70	78	76	+2	7.2	8.68	78	+1
240	4	18.9	6.8	8.69	76	74	+2	6.6	8.66	74	—1
255	5	2.0	6.4	8.67	72	71	+1	6.0	8.64	71	—1
270	5	9.2	5.8	8.65	69	69	0	5.4	8.62	68	—2
285	5	16.4	4.7	8.62	65	66	—1	4.9	8.61	66	—1
300	5	23.8	3.7	8.59	60	62	—2	4.2	8.58	62	—1
315	6	6.7	2.9	8.56	56	57	—1	3.6	8.57	60	+2
330	6	13.9	2.1	8.54	54	54	0	3.0	8.55	58	+3
345	6	21.1	1.5	8.52	51	51	0	2.4	8.53	55	+3
Mean . .							±1.3				±1.8

comparison stars of  $\delta$  *Cephei*, and the logarithms of two of these he found differed by only one hundredth of a unit. Accordingly, we can do no better than to draw a straight line nearly through the points designated by these stars, or assume that the value of a grade is constant. The columns of Table IX. have the same meaning as the corresponding columns of the previous similar tables.

TABLE IX.—COMPARISON STARS FOR  $\delta$  CEPHEI.

Name.	Wolff.	Grades.	Curve.	<i>W</i> — <i>C</i>	Grades.	Curve.	<i>W</i> — <i>C</i>
$\zeta$ Cephei . .	8.84	11.4	8.84	.00	12.4	8.86	—0.02
$\gamma$ Cephei . .	8.83	10.8	8.82	+0.01	10.9	8.82	+0.01
$\eta$ Lacertæ . .	...	7.1	...	..	6.6	..	..
$\epsilon$ Cephei . .	...	8.0	...	..	...	..	..
$\delta$ Cephei . .	8.53	2.0	8.53	.00	1.9	8.53	0.0

Table X. compares the various light curves with theory. The columns have the same meaning as those of Table V. The theoretical values are computed by the formula,  $L = 72.1 + 20.0 \sin (v - 45^\circ) + 7.0 \sin (2v - 120^\circ)$



TABLE X.—VARIATION IN LIGHT OF  $\delta$  CEPHEI.

v.	Time.	Argelander.			Oudemans.			Schönfeld.			Mean.	M A	M O	M S	Comp.	M—C
		Gr.	Log.	Obs.	Gr.	Log.	Obs.	Gr.	Log.	Obs.						
0	d. h.															
0	0 0.0	2.8	8.56	55	3.4	8.58	55	3.0	8.56	58	56	-1	-1	+2	52	+4
15	0 5.4	3.0	8.56	55	3.2	8.57	54	3.1	8.57	59	56	-1	-2	+3	55	+1
30	0 10.7	3.5	8.57	56	3.3	8.57	54	3.5	8.58	60	57	-1	-3	+3	61	-4
45	0 16.1	4.7	8.62	63	5.3	8.64	63	4.6	8.61	65	64	-1	-1	+1	69	-5
60	0 21.5	6.5	8.68	72	7.5	8.71	74	6.6	8.68	76	74	-2	0	+2	77	-3
75	1 2.8	8.4	8.74	83	10.3	8.81	93	8.7	8.75	89	88	-5	+5	+1	86	+2
90	1 8.2	9.9	8.79	93	11.1	8.83	98	10.0	8.79	98	96	-3	-2	+2	92	+4
105	1 13.6	10.7	8.82	100	11.2	8.84	100	10.4	8.80	100	100	0	0	0	96	+4
120	1 19.0	10.1	8.80	96	10.9	8.83	98	10.0	8.79	98	97	-1	+1	+1	98	-1
135	2 0.3	9.0	8.76	87	10.4	8.81	93	9.3	8.76	91	90	-3	+3	+1	96	-6
150	2 5.7	8.5	8.75	85	9.6	8.78	87	8.6	8.74	87	86	-1	-1	+1	91	-5
165	2 11.1	8.4	8.74	83	8.6	8.75	81	8.0	8.72	89	82	+1	-1	+1	86	-4
180	2 16.4	8.3	8.74	83	7.7	8.72	76	7.3	8.72	89	81	-2	-5	+2	80	+1
195	2 21.8	7.8	8.72	79	6.8	8.69	71	7.6	8.71	81	77	-2	-4	+4	75	-2
210	3 3.2	7.1	8.70	76	6.2	8.67	68	6.8	8.69	75	74	-2	-3	+4	71	-3
225	3 8.5	6.3	8.67	71	5.6	8.65	65	6.2	8.67	74	70	-1	-5	+4	69	+1
240	3 13.9	5.6	8.65	68	5.0	8.63	62	5.6	8.65	71	67	-1	-5	+4	67	0
255	3 19.3	5.2	8.64	66	4.4	8.61	59	5.1	8.63	68	64	-2	-5	+4	66	-2
270	4 0.6	4.7	8.62	63	4.0	8.60	58	4.7	8.62	66	62	+1	-4	+4	64	-2
285	4 6.0	4.3	8.61	62	3.7	8.59	56	4.2	8.60	63	60	+2	-4	-3	62	-2
300	4 11.4	3.9	8.59	59	3.6	8.58	55	3.9	8.59	62	59	0	-4	-3	59	0
315	4 16.7	3.4	8.58	58	3.6	8.58	55	3.6	8.58	60	58	0	-3	-2	56	+2
330	4 22.1	3.2	8.57	56	3.6	8.58	55	3.3	8.57	59	57	-1	-2	-2	53	+4
345	5 3.5	2.9	8.56	55	3.5	8.58	55	3.1	8.57	59	57	-1	-1	+3	51	+6
Mean . .											±1.4	±2.9	±2.8	..	±2.8	

These residuals are not large, considering the differences between the different observed values. There is, however, a curious alternation of the positive and negative signs. As a similar alternation appears in some of the other residuals, it is important to compare them to see if they can be shown to follow any law. There appear to be three maxima and three minima, or the variation repeats itself at intervals of about  $120^\circ$ . We should then exaggerate this effect by adding each set of the three residuals differing by  $120^\circ$ ; that is, the residuals corresponding to  $0^\circ$ ,  $120^\circ$ , and  $240^\circ$ , to  $15^\circ$ ,  $135^\circ$ , and  $255^\circ$ , etc. This is done in Table XI., in which the first value of  $v$ , in each set, is given in the first column, and the sums of the three residuals for the four stars are given in the second, third, seventh, and eleventh columns. The residuals of  $\zeta$  *Geminorum* are so small that we should expect no evidence of systematic error. In the other three cases marked variations are shown. In each case there are only two changes of sign, while there should be on the average four if the variations were accidental. The residuals of  $\beta$  *Lyrae* are well represented by subtracting from the computed value  $3 \cos 3v$ . The residuals which then remain are given in columns four, five, and six. Their average value is 1.6 instead of 2.8, or they have been reduced nearly one half. The residuals of  $\eta$  *Aquilæ*, in like manner, leave 1.1 instead

of 1.8, by subtracting the term  $3 \sin (3v - 45^\circ)$ . Those of  $\delta$  Cephei become 1.4 instead of 2.8, if we subtract  $4 \sin 3v$ .

TABLE XI. — TERMS INVOLVING  $3v$ .

$v$ .	$\zeta$ Gemine.	$\beta$ Lyræ				$\eta$ Aquilæ.				$\delta$ Cephei.			
		Sum.	Residuals.			Sum.	Residuals.			Sum.	Residuals.		
0	0	-9	-4	0	+4	+5	0	+1	-3	+3	+4	-1	0
15	0	-9	-3	-1	+1	0	0	+1	-1	-7	+4	-3	+1
30	-2	-2	0	0	-2	-4	+2	0	0	-11	0	-1	-2
45	+1	+7	+2	-1	0	-4	+2	+1	+2	-11	-2	-1	+1
60	+1	+9	0	0	0	-8	-1	-2	+1	-2	-3	+1	0
75	-1	+9	0	+1	+2	-2	-2	-2	+2	+6	-1	-1	-1
90	0	0	-1	+3	-2	+6	-1	0	+1	+11	0	-1	0
105	-1	-6	-1	+6	-5	+7	0	+2	0	+11	+1	-2	+3
Mean . .			$\pm 1.6$				$\pm 1.1$				$\pm 1.4$		

No natural explanation can be offered for such terms, and the reduction might be thought accidental did it not occur in so many different curves. A careful distinction must be made between these terms and those which might be assumed empirically, since their form is clearly pointed out by the residuals. If we tried to represent the residuals by a function of  $4v$ , we should soon see that the effect was wholly different, nor would any values of the arbitrary constants in this case materially reduce the residuals.

Neglecting these last terms, as their reality may be questioned, we may write the equations of the four stars under each other thus: —

$$\zeta \text{ Geminorum, } L = 89.6 + 10.2 \sin (v - 11.3^\circ)$$

$$\beta \text{ Lyræ, } L = 81.1 + 4.1 \sin (v - 90^\circ) + 20.0 \sin (2v - 90^\circ)$$

$$\eta \text{ Aquilæ, } L = 74.6 + 20.0 \sin (v - 60^\circ) + 6.0 \sin (2v - 120^\circ)$$

$$\delta \text{ Cephei, } L = 72.1 + 20.0 \sin (v - 45^\circ) + 7.0 \sin (2v - 120^\circ)$$

To compare them, it will be convenient to make the mean brightness equal to unity in all cases, or to divide by  $a$  the equation  $L = a + m \sin (v + \alpha) + n \sin (2v + \beta)$ . Instead of making  $v = 0$ , when the light is a minimum, it will also be better to take as the starting-point the position in which the shorter axis of the star is turned towards the observer. If  $v' = v + \gamma$ , we may write  $L' = 1 + m' \sin (v' + \alpha') + n' \cos 2v'$ . The various values of these constants are given in Table XII., which contains in successive columns the name of the star, the value of  $\gamma$ , of  $\alpha'$ , of  $m'$ , and of  $n'$ . Independently of the form of the star, its light would vary, owing to the unequal bright-

ness of the two sides from  $1 + m'$  to  $1 - m'$ . The brightness of the darker side would therefore equal  $\frac{1 - m'}{1 + m'}$  times that of the brighter.

In like manner, if the surface was uniformly bright, the variation in area of the disk, or the length of the shorter axis in terms of the longer, would be  $\frac{1 - n'}{1 + n'}$ . These quantities are given in the sixth and seventh columns. The last two columns give the average residuals in percentages before and after applying the terms which are functions of  $3v$ .

TABLE XII.—COMPARISON OF LIGHT CURVES.

Name.	$\gamma$	$a'$	$m'$	$n'$	$\frac{1 - m'}{1 + m'}$	$\frac{1 - n'}{1 + n'}$	Av. Resid.	Av. Resid.
$\zeta$ Geminorum	- 11.3	0	+ .114	..	0.80	..	0.5	..
$\beta$ Lyrae . . .	- 90.0	0	+ .051	+ .247	0.90	0.60	2.8	1.6
$\eta$ Aquilæ . . .	-105.0	+45	+ .268	+ .080	0.58	0.85	1.8	1.1
$\delta$ Cephei . . .	-105.0	+60	+ .277	+ .097	0.57	0.82	2.8	1.4

From the column  $\frac{1 - m'}{1 + m'}$  we see that in every case the darker side is more than half as bright as the other, and that the difference in the case of  $\beta$  Lyrae amounts only to ten per cent. In other words, if this effect is due to spots, we must conclude that they cover only one-tenth of the hemisphere in the case of  $\beta$  Lyrae, and about two-fifths in the cases of  $\eta$  Aquilæ and  $\delta$  Cephei. The next column also shows that  $\beta$  Lyrae is much elongated, the ratio of its axes being as five to three, while the two stars following have this ratio about as six to five.

The dark portion of  $\beta$  Lyrae is at one of the ends, since  $a' = 0^\circ$  for this star; it appears also to be symmetrically situated as regards the longer axis. The dark portions, both of  $\eta$  Aquilæ and of  $\delta$  Cephei, are placed somewhat preceding an end, that is, they are turned towards the observer before the end has been directed to him. For this reason the time from minimum to maximum is greater than that from maximum to minimum. This is probably a general law of stars of this class, as it has been noticed in several other instances.

One source of systematic error has been disregarded in the above comparison of observation with theory. In the value of  $L'$  the term  $m' \sin (v' + a')$  may be regarded as the measure of the effect of the difference in brightness of the two sides, and  $n' \cos 2v'$  as due to the form of the body. Their combined effect, however, would not strictly equal their sum, but would be found by adding each to unity and

taking the products of these sums. The actual light would equal  $(1 + m' \sin (v' + a')) (1 + n' \cos 2 v') = 1 + m' \sin (v' + a) + n' \cos 2 v' + m'n' \sin (v' + a) \cos 2 v'$ . The value of  $I'$  given above is then subject to the systematic error of  $m'n' \sin (v' + a) \cos 2 v'$ . The maximum value of this would equal  $m'n'$ , and it would generally be much less. The maximum value for  $\beta$  *Lyræ* would be about 1 per cent; for  $\eta$  *Aquilæ*, 2; and for  $\delta$  *Cephei*, 2.6 per cent. If the star underwent much greater change of light, it might be necessary to take this term into account; but in the present case it does not seem to sensibly affect the average value of the residuals.

Various attempts have been made to determine the light curve of  $\beta$  *Lyræ* photometrically. The observations of Zöllner and Wolff are reduced according to the same method in the photometric work of the latter, p. 110. The accuracy of the results does not make this a promising method of determining the light curve, unless the number of observations is greatly increased. The maxima and minima were also determined at the Harvard College Observatory.\* Calling the light at either maximum 100, that at the two minima would be 55.8 and 64.7, which agrees very closely with that given by computation, if we neglect the term  $3 \sin 3 v$ .

One great advantage of the study of the stars by physical instruments, such as the spectroscope and photometer, is that some clew is given to certain laws, for our knowledge of which we must otherwise depend on theoretical considerations alone. While the conclusions to be drawn from micrometric measurements are in general much more precise, and the effect of the errors can be more certainly computed, they fail entirely to aid us in studying such laws as those here considered. For example, the present investigation serves to study the following important problem in cosmogony, to which micrometric measures contribute nothing, and which can otherwise only be examined from the standpoint of theory. If we admit a common origin to the stars of the Milky Way, a general coincidence in their axes of rotation seems not improbable, especially as such an approximate coincidence occurs in the members of the solar system. If the coincidence was exact, the direction must be that of the poles of the Sun, or, approximately, that of the pole of the ecliptic. On the other hand, since the stars of the Milky Way are supposed to be arranged in the general form of a flattened disk, we should more naturally expect that the axes of rotation would be symmetrically situated with regard

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\* *Annals*, xi. 135.

to it, or would coincide with its shortest dimension. According to this theory, then, the axes of rotation would be directed towards the poles of the Milky Way. If now we suppose that a great number of variable stars, of the form described above and rotating around parallel axes, were distributed over the heavens, it is evident that those seen in the direction of their axes would not appear to vary, since as they turned they would always present the same portion of their surfaces to the observer. Those at right angles to this direction would show the greatest variation, and, other things being equal, would appear to be more numerous since they would be more likely to be detected. If then the axes are coincident, we should expect that most of these variable stars would lie along the arc of a great circle whose pole would coincide with their axes of rotation. An inspection of a plot of the stars of Class IV. showed that they agreed closely with a great circle whose pole is in R. A.  $13^h$  and Dec.  $+20^\circ$ . To compare these stars in this and in other respects, they are arranged in the order of their periods in Table XIII. They are divided into three sections; first, those known to be of the fifth class; secondly, those of the fourth class, including all of a shorter period than  $\beta$  *Lyræ*; thirdly, the remaining variables of longer period, whose position in Class IV. may be open to question. The first column gives the name of the star, and the second its period in days. The distance from the great circle whose pole is in R. A.  $13^h$  and Dec.  $+20^\circ$  is given in the third column. It was found by measurement on a globe, instead of by calculation, and is not therefore exact to the nearest degree.

In measuring the stars of the fifth class at the Harvard College Observatory, much difficulty was experienced from the absence of adjacent comparison stars. Stars of the fourth class, on the other hand, have, in almost all cases, stars near them. An unprejudiced comparison is made in the next two columns, by giving the magnitude and distance, in minutes, of the nearest star of the *Durchmusterung*. The lines for the southern stars are therefore left blank. If the stars of the fourth class lie near the Milky Way, we should expect an increased number of companions due to this cause. Accordingly, a count has been made of the *Durchmusterung* stars in a square degree, in which each star is contained. This area is defined as the portion of the *Durchmusterung* zone in which the star is situated, having an average length of one degree, one half preceding, the other half following, the variable. The results are given in the sixth column. If these stars were connected with the variables, we might expect that they would lie, approximately, in a plane at right angles to the axes of rota-

TABLE XIII.—COMPARISON OF VARIABLE STARS.

Class V.							
Name.	Period.	Dist.	Mag.	Dist.	No. Stars.	Ang.	Birm.
$\delta$ Libræ . . .	2.32	+51	..	..	..	0	..
— Cephei . . .	2.49	+11	9.5	5.1	20	..	..
$\beta$ Persei . . .	2.87	-24	8.8	7.5	15	..	55
$\gamma$ Coronæ . . .	3.45	+58	9.4	11.5	7	..	..
$\lambda$ Tauri . . .	3.95	-41	9.5	17.5	6	..	..
$S$ Cancri . . .	9.48	+25	9.1	11.6	16	..	..
Mean . . . . .		$\pm 35^\circ$	..	10'.6	12.6	..	..
Class IV.—Short Periods.							
$R$ Muscæ . . .	0.89	0	..	..	..	..	..
$T$ Triang. Austr.	1.00	+3	..	..	..	..	..
— Sagittarii . .	2.42	-1	..	..	..	..	..
$S$ Monocerotis .	3.40	-4	9.4	1.0	29	-31	..
$R$ Triang. Austr.	3.40	+1	..	..	..	..	..
$N$ Velorum . . .	4.25	+1	..	..	..	..	..
$\delta$ Cephei . . .	5.87	-5	7.5	1.5	31	-33	..
$S$ Coron. Austr..	6.20	-9	..	..	..	..	..
$U$ Sagittarii . .	6.75	+2	..	..	..	..	445
$X$ Sagittarii . .	7.01	+8	..	..	..	..	..
$\eta$ Aquilæ . . .	7.18	-9	9.2	3.2	17	+20	..
$W$ Sagittarii . .	7.59	+3	..	..	..	..	..
$\kappa$ Pavonis . . .	9.10	-16	..	..	..	..	..
$\zeta$ Geminorum . .	10.16	+5	8.5	1.8	33	+1	..
$\beta$ Lyræ . . . .	12.91	+14	8.5	1.5	34	-20	..
Mean . . . . .		$\pm 5^\circ$	..	1'.7	28.8	$\pm 21^\circ$	..
Class IV.—Long Periods.							
$W$ Virginis . . .	17.27	+66	..	..	..	..	284
$T$ Monocerotis . .	27.00	-8	9.5	6.1	23	0	..
$\iota$ Carinæ . . .	31.25	-1	..	..	..	..	..
$\eta$ Herculis . . .	38.50	+34	9.4	5.0	15	+79	405
$U$ Monocerotis . .	46.00	+2	..	..	..	..	..
$R$ Lyræ . . . .	46.00	+16	7.1	9.7	17	-78	474
$R$ Coron. Austr..	54.00	-9	..	..	..	..	..
$S$ Vulpeculæ . . .	67.50	0	9.5	5.2	20	+53	517
$R$ Sagittæ . . .	70.42	-9	9.3	5.0	26	+76	540
$R$ Scuti . . . .	71.10	+3	..	..	..	..	462
Mean . . . . .		$\pm 13^\circ$	..	6'.2	20.2	$\pm 57^\circ$	..

tion, since the planes of revolution of the planets do not differ greatly from the solar equator. Moreover, if the elongation of the variable was caused by one or more disturbing bodies, we should expect that they would lie in this plane. Of course, the present distance of these

companions is far too great to sensibly affect the variables, but other nearer objects may lie in the same plane. The approximate position angle of the companion was computed from its *Durchmusterung* place. The position angle of the pole of the variable stars was measured by a protractor, laid upon the globe over the position of the variable star, and stretching a thread to the pole. Each of these determinations is liable to an error of some degrees, but the results which are given in column seven are sufficiently exact for our present purposes. Some of these stars are red, and when they are contained in the Catalogue of Birmingham\* their numbers are given in the last column.

The numbers of the third column show that the stars of the fifth class are not concentrated in the assumed plane. If uniformly distributed all over the heavens, their average distance should be about  $30^\circ$ , since one half of each hemisphere is contained in a zone of this width. In the short-period stars of the fourth class, however, the agreement is most remarkable. None have yet been found more distant than  $16^\circ$  from the circle, and with two exceptions none are more distant than  $10^\circ$ . There is only one chance in four that a given star should lie within  $15^\circ$  of a given great circle, and about one in six that it should lie within  $9^\circ$  of it. Evidently the chances would be many millions to one against the observed arrangement being accidental. As an argument in favor of the parallelisms of the axes, this distribution of the stars fails by proving too much. We should expect, if the axes were parallel, to find nearly as many stars between  $10^\circ$  and  $20^\circ$ , as between  $0^\circ$  and  $10^\circ$ , since the variation would be a function of the cosines of these angles. If the axes were not exactly coincident, we should find the stars still more widely distributed.

Of course it is possible that the distribution of these stars may be partly due to the parallelism of their axes of rotation. But we have shown that the latter cause is insufficient. Since then we must assume an arrangement of the stars approximately in a plane, we cannot be sure that their apparent distribution is not wholly due to it, and the evidence in favor of parallelism of their axes is much weakened.

It is a little singular that this plane appears to pass through the Sun. We should expect that while the more distant stars might lie upon a great circle, the nearer, and therefore presumably the brighter, stars, would lie on the opposite side of it from the Sun. As, however, the positive and negative signs are nearly equally distributed, we must

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\* Trans. Roy. Inst. Acad., xxvi. 249.



infer that the distance of the Sun from the plane of these stars is small compared with its distance from them. If the stars lay exactly in one plane we might infer their distances from the Sun from these residuals. As the residuals of the brighter stars show no systematic arrangement, it seems probable that the variables of the fourth class lie nearly, but not exactly, in a plane. This plane approaches that of the Milky Way, but does not coincide with it. The pole of the latter is nearly in R. A.  $12^h 40^m$  and Dec.  $+28^\circ$ . Evidently the residuals in column three would be greatly increased if we moved the pole from its assumed position of R. A.  $13^h$  and Dec.  $+20^\circ$ , by more than  $10^\circ$  to the pole of the Milky Way. The position of the Milky Way, as given in the "Atlas Coelestis Novus" of Heis, agrees, however, more closely with the plane of the variable stars.

It is not certain whether the stars of longer period given in the third section of Table XII. should be included with those of the fourth class of variables. With two exceptions, *W Virginis* and  *$\alpha$  Herculis*, they lie near the plane of the others.

The total number of stars in the Durchmusterung north of the equator is 315,048. Since the area of the hemisphere is 20,626 square degrees, this corresponds to 15.3 stars per degree, or an area of 236 square minutes to each star. A circle having a radius of  $8'.7$  would have an area equal to this. If, then, a circle having this radius is described around any star as a centre, it will be an even chance that another star will be contained within it, provided that the presence of the second star is no way affected by that of the first. For circles of other radii the chances will vary as the squares of the radii, or as the areas. We know from the existence of clusters and multiple stars that one star is not without influence on the presence of another, and that this effect may extend to some distance, as is shown in the Pleiades and in Praesepe. This principle may still be used in comparing different classes of stars, although the distance  $8'.7$  should be diminished. It is, therefore, surprising that the average distance of the companions of stars of the fifth class is as great as  $10'.6$ , especially as two of them, *S Cancri* and  *$\lambda$  Tauri*, lie near the large clusters Praesepe and the Hyades, where the average intervals between the stars is much less. A circle of radius  $10'.6$  has only two-thirds the area of that of  $8'.7$ , hence these companions are only two-thirds as thickly placed as the stars in other parts of the heavens. This effect extends to the square degree, as is shown in the sixth column. It appears to be probable that there is no physical connection of these stars with the variables, and that their sparseness is due to their distance from the Milky Way.



Passing now to the second part of the table, we find a wholly different condition of things. Every star has a companion near it at an average distance of only  $1'.7$ , or these stars are twenty-six times as thickly placed as in the rest of the heavens, since  $8.7^2 : 1.7^2 = 26 : 1$ . This effect is partly due to the surrounding square degree, which contains nearly double the average number of stars. Only a small part of this effect may, however, be thus explained. We may, therefore, infer that there is a physical connection between these variables and their companions, or that they are at nearly the same distance from the Sun, and not optically double. The singular character of these stars renders them interesting objects for the measurement of parallax. This is especially the case with those of very short period, since from the rapidity of the changes we might infer that they were really small, and therefore near. Now an observer would be very likely to select the companions as points to measure from, since their distances are much greater than that separating the components of most stars which are binary, or are supposed to be physically connected. A measurable parallax might thus escape detection.

The stars of longer period occupy an intermediate position as regards the distances of the components, and the number of stars in the square degree.

If the direction of the components depended wholly on chance, we should find that they would differ, on the average, from that given by any theory, by about  $45^\circ$ . It therefore seems scarcely probable that, in each of the five cases, a chance distribution would give the angle less than  $45^\circ$ , for the stars of short period. The uncertainties in the measurements would in general increase the discrepancies, so that it is to be expected that a more accurate determination would diminish the mean value, although it would doubtless alter the separate results by many degrees. The position of the components of the stars of the fifth class has not been determined, as it seems very improbable that they have any physical connection. The stars of long period, with one exception, give results which do not agree at all with theory. Some more precise test of the class to which these variables should be assigned, is therefore much needed. They are distinguished from many of the stars of the second class only by the length of their period, no other known variables having a period less than that of *R Vulpeculæ*, or 137 days. Stars of Class II. have banded spectra, and are of a red color. This suggested a test dependent upon observations already made. The last column shows what stars have been regarded as red, and may, therefore, in some cases belong to Class II. The only

star of Class V. given in Birmingham's Catalogue is  $\beta$  *Persei*, and many observers may be surprised that this should have been called a red star. It is remarkable that but one star of short period, *U Sagittarii*, is called red. On the other hand, six of the variables of long period are given in the catalogue, including all of those which have shown marked discrepancies. Excluding these disposes of the large deviations,  $66^\circ$  and  $34^\circ$ , in column three; and we find no star more distant than  $16^\circ$  from the assumed plane in which the variables lie. Again, the large discrepancies of the last column but one are removed, and *T Monocerotis* probably placed with the variables of the fourth class. This view is confirmed by the light curve given by Schönfeld, page 32 of the catalogue cited above, which shows that in the form of its variations this star closely resembles  $\eta$  *Aquilæ* and  $\delta$  *Cephei*. Another reason for excluding *W Virginis* and the last four stars of the list is, that their light is variable at their maxima, and in four of the five cases at their minima. This frequently happens with stars of Class II., but would not be readily explained in stars of Class IV.

The Uranometria Argentina adds *U Monocerotis* to the list of red stars. All stars whose period lies between 32 and 72 days have, therefore, been called red, except *R Coronæ Australis*. This star is so faint that its color might well have been overlooked.

A further discussion would have been made of *T Monocerotis*, but no means exist for converting into light ratios the scale of magnitudes of its light curve. As the brightness of the comparison stars are not given, we have no means of knowing whether a tenth of a magnitude corresponds to the same light ratio when this star is faint, as when it is bright. A preliminary trial showed that the maximum appeared to occur more suddenly, and the minimum more slowly, than theory would indicate. The large range of variation of this star renders it well suited for study, and the same may be said of some others of the list, as a slight increase in the difference between the maximum and minimum greatly increases the severity of the test the light curve offers to theory.

The system which appears to govern the position of the companions to these stars suggests an investigation which might lead to important results. The planes of the orbits of the binary stars are defined by their inclination and the position angle of the node. Since we cannot determine micrometrically the direction in which the orbit is inclined, we can only say that the pole of this orbit lies in one of two places. Should any law be discovered, we might then decide for any particular star what sign should be given to the inclination, and also whether the

motion was direct or retrograde. It might also help to determine the amount of the inclination when the latter is not large enough to be determined precisely by micrometric measurements. Such a law would render an important aid to the study of the orbits of the dark companions of stars of the fifth class. They would afford a check on the observed inclination, and would define the position angle of the major axis of the orbit, which is now wholly indeterminate. An inspection of the orbits of the binaries fails to show any law, but it is possible that this might be brought out by a more careful examination, as has been done with the proper motion of the stars. The conclusion regarding the motion of the Sun in space is liable to large error, in case systematic errors exist in the catalogues on which the positions of the stars depend. Such an error in Bradley might greatly change the conclusion generally accepted. The orbits of the binaries, on the other hand, are wholly independent of each other, and there is little danger of a systematic error affecting all.

The elegant method of Argelander for determining the light curve of the variable stars leaves little to be desired as a means of determining their periods and the times of their minima. Its simplicity, and the need of no instrument but a telescope powerful enough to show the variable, are strong arguments in its favor when comparing it with the best photometric methods. If, however, we wish to determine the true light curve, the following sources of error become perceptible. As the comparison stars are selected from the immediate neighborhood of the variable, they are few in number; and if any one of them proves to be itself variable, the errors introduced are large. It is difficult to obtain independent estimates, since there is but little range of choice in the star to be selected at any given time. Much skill is required on the part of the observer to make a grade the same when the variable is bright as when faint, to make it the same on different nights, and to make the interval of two grades double that of one. In reducing the light to logarithms, it appears to be impossible to render the errors of the measures of the comparison stars as small as those of the light curves. The comparisons given above show that the errors of the measurements of the comparison stars probably exceed those from all other sources combined.

Three methods may be used for determining the brightness of the stars without a photometer. First, the observer may keep a certain scale in mind, and by it estimate the light of the stars in tenths of a magnitude. He should first estimate several known stars, and compare his result with their true brightness, so as to apply mentally to his

scale proper corrections for the effect of haze, moonlight, etc. He may also observe a large number of known stars, and afterwards reduce his scale for the evening from a discussion of their light.

In the second method, which is that of Argelander, the observer selects a comparison star of very nearly the same light as the star to be measured, and estimates the difference in grades, a grade being a small interval nearly equivalent to a tenth of a magnitude. A discussion of all the observations serves to determine the intervals in grades between the comparison stars. The value of one grade is then determined from photometric measures of the comparison stars. According to the third method, the observer selects two comparison stars, one a little brighter, the other a little fainter, than the star to be observed, and estimates its difference in magnitudes from the brighter component, with the difference between the two comparison stars. The first of these methods is the most rapid, and is well adapted to zone observations, or to any work with a meridian instrument. More skill is, however, required on the part of the observer than by either of the other methods. Besides being able to judge of small intervals of brightness, as in the other methods, he must be able to prevent any changes from taking place in his scale, at least during a single evening. The second method requires less skill, since the observer must merely keep the values of his grades constant; but in the third method even this is not needed. It is, therefore, probably the most exact, when the results are to be reduced by photometric measures of the comparison stars. The three methods are directly comparable with those which may be used in estimating linear measures. We may estimate the length of a bar directly in inches, or its excess in inches over a similar bar of known length; or, thirdly, we may compare it with two bars, one a little longer, the other a little shorter, and estimate its relative length compared with them. It can hardly be doubted that the last of these methods would give the most accurate results. When applied to the stars, the third method has also an advantage in reducing the accidental errors of the photometric measures, since the comparison is made with two stars instead of one.

The light curve of a variable may then be determined as follows:—Select as comparison stars all those of nearly the brightness of the variable, and not too far distant, excepting any which may be thought to be variable, to differ from the variable in color, or which are near other stars. Photometric measures should be obtained, during the period over which the observations of the variable extend, of all of those stars which are used. Each star should be measured in turn under precisely the same conditions, by a Zöllner photometer or other

instrument, and this should be repeated on several evenings. The relative light will thus be obtained with great accuracy, as the same errors will be likely to affect them all. If this cannot be done, the Uranometria Argentina, with the measures now in progress at the Harvard College Observatory, will give the brightness of all the naked-eye stars, with an error probably less than a tenth of a magnitude.

The light of the variable would be found by selecting two comparison stars, one a little brighter, the other a little fainter than it, and comparing the interval between the variable and the brighter, with that between the two comparison stars, which may be assumed equal to 10. Thus,  $a \ 4 \ b$  will denote that the interval between the bright comparison star  $a$  and the variable is estimated at only four-tenths of that between the two comparison stars. Of course the time of each comparison must be recorded. This measure should be repeated with different pairs of comparison stars. Thus, if  $a$  and  $b$  are brighter and  $c$  and  $d$  fainter than the variable, we may compare the latter with  $ac$ ,  $ad$ ,  $bc$ , and  $bd$ . In like manner, with six comparison stars we may obtain nine independent measures. The reduction is very simple, since it is useless to carry the estimates beyond tenths of a magnitude.

The above paper has suggested several researches of importance, and which are accordingly placed together below : —

1. Determination of the light curves of any of the variables of short period, except  $\beta$  *Persei*,  $\zeta$  *Geminorum*,  $\beta$  *Lyræ*,  $\eta$  *Aquilæ*, and  $\delta$  *Cephei*, for which satisfactory curves have already been obtained. The method of Argelander, or that proposed above, may be used with advantage.

It must be remembered that the observations will have little value, unless they are reduced and the light curve found. A vast number of excellent observations of these stars already exist, including the larger part of those of Argelander, which will have no value until they are reduced.

2. Determination of the light curve of the stars of the fourth class photometrically. This may be done with great accuracy by an instrument similar to that described in the Annals of the Harvard College Observatory, xi. 4, Figs. 1 and 2. The proximity of the companions render these objects especially suitable for photometric measurement.

3. Photometric measures of the comparison stars used in (1), of those used by previous observers, and the reduction of the observations by these measures to light intensities.

4. Search for variables of the fourth class, selecting from the Durchmusterung those fulfilling the conditions named above. They may be readily identified by their companions, and observed very rapidly by a

transit instrument, or small equatorial. The first of the three methods of estimating their light is to be recommended for this work. It is sufficiently precise, and the scale used each evening would be readily found from the *Durchmusterung* magnitudes of the great mass of the stars which would, probably, be invariable in light. Any interesting variable would be detected by observations on a few nights.

5. Measures of the position angles, distances, and magnitudes of the companions. The approximate places given from the *Durchmusterung* in Table XIII. could thus be corrected, and the blanks for southern stars filled. The magnitudes could best be measured by the photometer recommended in (2). Otherwise especial care should be taken that the light of the fainter star was not affected by the proximity of the brighter.

6. Observations of the color and spectrum of these stars, to decide which ones, if any, should be included in the second class.

7. Distribution of the light in the spectra of these stars, and also of those of the second class at their maxima and minima.

8. Computation by Jacobi's method of the true diameter of a liquid ellipsoid in equilibrium, having given the period of rotation and the ellipticity of the equator.

9. Computation of the Galactic latitude and longitude (or distance and direction from the pole of the Milky Way) of variables of Classes II. and IV., of the planetary and other gaseous nebulae, and of stars whose spectrum is of the fourth type.

10. Computation of the position of the poles of the orbits of the binary stars.

The object of the present paper is not to advocate a certain theory which may seem improbable, and, possibly to some, inadequate. It is rather intended to bring together the most important facts bearing on the study of an interesting class of objects, and to exhibit them in a form in which they may be subjected to any desired test. The hypothesis advanced has a value as affording a simple geometrical conception of the nature of the variations under consideration, even if it proves not to be the true explanation of the cause. The ingenious hypothesis of Zöllner, and other explanations of these phenomena, have not been overlooked. It seemed best, however, to leave to another to decide the comparative merits of views in which the precision of the effects must be considered as well as the probability of the causes.

One theory, that the variation is due to the absorption of a rotating mass of gas, deserves a moment's consideration. This explanation does not appear probable for stars of the fourth class, since no evidence



of absorption is in general shown in their spectra beyond the appearance of lines such as are seen in our Sun. For the stars of the second class, however, this view seems more reasonable, since many of them exhibit spectra which are strongly banded. Moreover, the great variation in light is thus explained. An excellent test of this hypothesis is afforded by the variation in light of the different portions of the spectra. For light of any given wave-length the logarithm of the transmitted ray will always vary proportionally to the thickness and density of the absorbing medium, the amount of absorbent effect for any given thickness varying with the wave-length. Accordingly, a study of the variation of each ray should show the same law. They would give very different coefficients of absorptions, those of the dark bands being large, and those of the bright zones being small. The great variation in light will render this test a severe one with even a moderate degree of accuracy in the observations. For the lack of any data, this method of study is for the present unavoidably postponed.

The principal conclusions of the above paper may be summarized as follows:—

Thirty-one variable stars are known whose period is less than 72 days. Of those six belong to the fifth class, or that of  $\beta$  *Persei*, in which the variation is probably due to the interposition of an opaque eclipsing satellite. Of the remainder, seven may be excluded, since they are red, and may belong to the second class, or that of  $\alpha$  *Ceti*. Nineteen remain, whose periods vary from less than a day to 54 days, and which may be placed in the fourth class. All lie within  $16^\circ$  of a great circle whose pole is in R. A.  $13^h$ , Dec.  $+20^\circ$ . The distances of eleven are from  $0^\circ$  to  $5^\circ$ , of five at distances  $8^\circ$  and  $9^\circ$ , one at  $14^\circ$ , and one at  $16^\circ$ . The average distance is  $5^\circ.5$ , while if the stars were distributed at random it should be  $30^\circ$ .

If the stars of the *Durchmusterung* were uniformly distributed, their average distance apart would be about  $8'.7$ . The five stars of the fifth class have *Durchmusterung* companions at an average distance of  $10'.6$ . In the fourth class, excluding the red stars, six are in the *Durchmusterung*, and have companions at an average distance of  $2'.5$ , four being less than  $2'.0$  distance, one at  $3'.2$ , and one at  $6'.1$ . In all six cases the direction of the companions is within less than  $34^\circ$  of the plane near which the variables lie, or at an average distance of  $18^\circ$ , while, if distributed by chance, this angle should be  $45^\circ$ . Hence a method of discovering variable stars of this class is offered by looking in a certain part of the sky for those having near companions in a given direction.

The light curves of four stars have been determined with sufficient precision to permit a comparison with theory. All of these may be represented by the formula  $L' = 1 + m' \sin (v' + a) + n' \cos 2v'$ , in which  $L'$  is the light when the star has turned through the angle  $v'$ . The difference between observation and theory amounts on the average to only about 0.03 of a magnitude. In other words, the light of these stars at any time may be computed with this degree of precision.

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## XIV.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XIV. EXPERIMENTS ON THE STRENGTH AND  
STIFFNESS OF SMALL SPRUCE BEAMS.

By F. E. KIDDER.

Presented by Prof. Charles R. Cross, Feb. 9, 1881.

THE object of the following experiments was to determine the Moduli of Elasticity and Rupture in small beams of white spruce (*Abies alba*); and such other information as might be derived from the data obtained.

The machine used for the purpose consists of two solid wooden frames, carefully levelled and placed forty inches apart. Upon the top of each frame is placed a movable plate of iron, which is carefully adjusted so that the two plates shall be directly opposite each other, and exactly forty inches apart between the faces. These plates form the supports for the beams.

The loads were applied by means of a scale pan suspended from a three-quarter inch bolt, which rested upon the centre of the beam. By means of an iron strap suspended from a horizontal beam placed above the test piece, and resting on two screws, the bolt from which the load was suspended could be raised from or lowered upon the test piece as easily and gradually as could be desired.

The deflections of the beams were measured by means of a micrometer screw, reading to one ten-thousandth of an inch. As the bolt from which the load was suspended rested on the centre of the beam, it was necessary to measure the deflections at a distance of one inch from the centre; but the deflections used in calculating the values of the Modulus of Elasticity were corrected so as to give the deflection at the centre, supposing the curve assumed by the beam to be the arc of a circle; from which, in fact, it deviates but little under such small

loads. In reading the micrometer, the principle of electrical contact was taken advantage of.

The greatest errors liable to occur in using the machine are as follows:—

In measuring the deflections, one ten-thousandth of an inch. In the breaking load, possibly one pound; but in the small loads there could be no appreciable error. In measuring the dimensions of the test pieces, two thousandths of an inch.

The experiments were conducted with the utmost care, and every possible precaution was taken to prevent errors.

In arranging for the experiments, and while making them, the writer was greatly assisted by Mr. Holman, of the Institute, to whom he extends his acknowledgments.

The pieces of wood experimented on were sawn from a spruce plank that had been cut in eastern Maine in the spring of 1880, and the following summer shipped to Boston, where it had lain in the open air until it was cut up in October. The pieces were carefully planed to an approximate size of one and a half inches square and four feet long.

They were nearly all straight-grained and had but few defects, and in testing the beams they were placed so that the defects should have the least possible effect upon the strength of the beams. The exact dimensions of the test pieces are given in Table I.

TABLE I.

No. of Test Piece.	Clear Span. <i>l</i> .	Breadth. <i>B</i>	Depth <i>D</i> .	<i>E</i> .	<i>E</i> <sub>1</sub> .	<i>R</i> .	Centre break- ing weight for beam 1" × 1" × 1'.
	ins.	ins.	ins.	lbs.	lbs.	lbs.	lbs.
1	40	1.475	1.450	1,731,000	1,657,000	11,380	632
2	"	1.445	1.520	1,556,000	1,528,000	10,330	574
3	"	1.469	1.448	1,765,000	1,732,000	10,710	595
4	"	1.420	1.498	1,736,000	1,636,000	10,830	601
5	"	1.450	1.485	1,688,000	1,578,000	11,980	665
6	"	1.480	1.440	1,795,000	1,686,000	11,040	613
7	"	1.464	1.460	1,682,000	1,561,000	10,570	587
8	"	1.420	1.480	1,647,000	1,556,000	11,280	626
9	"	1.460	1.460	1,704,000	1,638,000	11,180	621
10	"	1.441	1.460	1,616,000	1,550,000	12,440	691

In making the experiments, each beam was first subjected to a load of thirty pounds, and the deflection noted. The weight was then left on the beam for a period of time varying from one to four, and in one case forty-four hours, and the deflection again noted. The load was

then removed from the beam and the set noted, after which the beam was allowed a certain time to recover from the set.

After the piece had returned, or at least nearly returned, to its original position, it was subjected to a load of forty pounds in the same manner.

Table II. gives the deflection of each piece under the loads of thirty and forty pounds, both immediately after the weight was applied and after it had rested upon the beam the length of time designated.

TABLE II.

No. of Test Piece.	Weight W.		Time applied.		Deflection $\Delta$	E.	Weight W.	Time applied.		Deflection $\Delta$	E.
	lbs.	h. m.	ins.	lbs.			lbs.	h. m.	ins.		
1	30	0 00	0.0610	1,744,000	40	0 00	0.0826	1,719,000			
"	"	2 25	.0630	1,689,000	"	3 30	.0873	1,627,000			
2	30	0 00	.0616	1,536,000	40	0 00	.0801	1,576,000			
"	"	1 45	.0639	1,481,000	"	3 00	.0842	1,499,000			
3	30	0 00	.0606	1,774,000	40	0 00	.0815	1,757,000			
"	"	1 00	.0610	1,759,000	"	1 00	.0840	1,705,000			
4	30	0 00	.0582	1,725,000	40	0 00	.0765	1,748,000			
"	"	2 25	.0616	1,627,000	"	3 20	.0813	1,645,000			
5	30	0 00	.0580	1,740,000	40	0 00	.0774	1,637,000			
"	"	2 30	.0618	1,630,000	"	44 15	.0874	1,527,000			
6	30	0 00	.0605	1,792,000	40	0 00	.0803	1,799,000			
"	"	3 00	.0639	1,697,000	"	5 12	.0862	1,676,000			
7	30	0 00	.0624	1,683,000	40	0 00	.0833	1,682,000			
"	"	3 00	.0663	1,584,000	"	16 00	.0911	1,538,000			
8	30	0 00	.0632	1,645,000	40	0 00	.0839	1,650,000			
"	"	4 15	.0666	1,561,000	"	16 30	.0894	1,552,000			
9	30	0 00	.0619	1,701,000	40	0 00	.0823	1,707,000			
"	"	1 30	.0643	1,638,000	—	—	—	—			
10	30	0 00	.0661	1,614,000	40	0 00	.0881	1,618,000			
"	"	2 00	.0691	1,544,000	"	1 15	.0915	1,556,000			

The values of the Modulus of Elasticity calculated from these deflections are also given. The Moduli of Elasticity obtained from the deflection of the beams immediately after the weight was applied have been denoted by  $E$ , and those obtained from the deflection of the pieces after the weight had been applied one or more hours, by  $E_1$ . Table I. gives the values of  $E$  and  $E_1$  for each piece, obtained by taking the average of the values given in Table II.

The values of  $E$  were computed by the formula  $E = \frac{Wl^3}{4\Delta BD^3}$ , in which  $W$  denotes the weight in pounds producing the deflection;  $l$  the clear span in inches;  $\Delta$  the deflection of the beam at the centre;  $B$  the breadth of the beam, and  $D$  the depth, both in inches.

After all of the beams had been treated in this way, piece No. 3 was again put in the machine and subjected to a load of 100 lbs.,

which was allowed to remain upon the beam for about two hours, the deflection being measured directly after the weight was applied and just before it was removed. The beam was then allowed a certain time to recover its set. In two cases, the beams, after having been subjected to a load of 100 lbs., finally returned to their original position, and it appeared probable that all would have done so had sufficient time been allowed for the purpose.

After the piece had nearly recovered from the effects of the load of 100 lbs., a load of 150 lbs. was put on the beam, and gradually increased until the breaking point was reached.

The remaining pieces were tested with a load of 100 lbs. in the same way, and then subjected to a load of 400 lbs. for one or two minutes, for the purpose of getting the deflection under that load, and immediately after subjected to the full load of 500 lbs., which was gradually increased until the piece broke. As the load approached the breaking weight, it was increased by the addition of only one or two pounds at a time, so that the breaking weight could be obtained with sufficient accuracy. In fact, the breaking weight is so much modified by the time occupied in breaking the beam, that it is difficult to ascertain exactly what it really is. For any load, over three-fourths of what is called the breaking weight would probably break the beam if applied long enough.

Table I. gives the values of the Modulus of Rupture of each piece, computed by the formula  $R = \frac{3}{2} \frac{Wl}{BD^2}$ , in which  $R$  denotes the Modulus of Rupture;  $W$  the breaking weight of the beam, and the other letters have the same significance as in the formula for  $E$ . The load which would break a beam of the same wood, one inch square and one foot between supports, if applied at the centre, is also given in the same table. This load is one eighteenth of the Modulus of Rupture.

When the weight of 400 lbs. was applied to piece No. 7, it immediately cracked at a knarl in one of the lower edges, about three-fourths of an inch from the centre of the beam. As it was thought that the beam would soon break entirely, the load of 400 lbs. was allowed to remain on the beam; but at the end of one hundred hours the deflection had only increased 0.2224 inches, and as it was evident that it would, at that rate, take a long time for the beam to break, the load was then gradually increased until the piece broke at 550 lbs., giving a Modulus of Rupture considerably above the average. It was noticed in this beam that the deflections under the loads above 500

lbs. were considerably greater than in the other beams under the same loads.

Piece No. 5 gave a very high breaking weight, and broke very suddenly, more like the harder kinds of wood. The fracture was very perfect, the upper half of the fibres being very evidently compressed and the lower half suddenly pulled apart, with almost no splintering. This piece had a small knot on the upper side, five inches from the centre of the beam, but it appeared to have no effect upon the strength of the beam.

Piece No. 4 broke in a rather peculiar manner. While under a load of 575 lbs., the lower fibres for about a depth of one-tenth of an inch snapped apart, and the beam gradually settled down until the next layer of fibres had apparently the same deflection as did the lower ones at the time of breaking, when they also snapped, making a layer of about the same thickness. In this way the whole lower half of the beam seemed to divide itself into layers of about one-tenth of an inch thick, and to break separately under about the same deflection, so that the beam was a long time in breaking.

Observing that under every load that had been applied the deflection kept increasing with the length of time the weight remained on the beam, piece No. 7 was subjected to a load of 275 lbs. for ninety-eight hours, during which time the deflection increased 0.079 inches. The weight was then taken off and the beam allowed to recover for twenty-four hours, when it had a set of .0446 inches. The same weight was again applied, and it was found that the deflection, obtained by taking the difference between the readings of the micrometer just before and after the weight was applied, was less than it was the first time the weight was applied, and the rate of increase of the deflection was about the same as before. The beam was thus subjected to a weight of 275 lbs. for three hundred hours in all, after which it was broken in the same manner as the others. It was expected that the effect of such a severe strain for so long a time would diminish its strength; but, on the contrary, it appeared to increase it, as the beam gave a higher Modulus of Rupture than any of the others, although it did not appear to be of as good quality as many of them. The ultimate deflection of this beam greatly exceeded that in any of the others.

Table III. shows the deflection of each beam under loads of 30, 40, 100, 400, 500, and 550 lbs., immediately after the load was applied, and at a distance of one inch from the centre. The small figures under each deflection show what it would be if Hooke's Law held true, taking the deflection under 30 lbs. as the starting-point.

TABLE III.

No of Test Piece.	Deflection in inches under						Ultimate Deflection.	Breaking weight. lbs.
	30 lbs.	40 lbs.	100 lbs.	400 lbs.	500 lbs.	550 lbs.		
1	0.0610	0.0826	0.2071	0.8303	1.0906	1.2791	1.5646	588
2	.0610	.0813	.2030	.8120	1.0150	1.1165	1.3941	575
	.0616	.0801	.2043	.8177	1.0677	1.2811		
3	.0616	.0820	.2050	.8200	1.0250	1.1275	1.4800*	550
	.0606	.0815	.2023	.8976	1.2764	1.4800*		
4	.0606	.0808	.2020	.8080	1.0100	1.1110	1.4658	575
	.0582	.0765	.1929	.7929	1.1146	1.3197		
5	.0582	.0776	.1940	.7760	0.9700	1.0670	1.5788	637
	.0580	.0774	.2004	.7876	1.0170	1.1827		
6	.0580	.0773	.1933	.7732	0.9665	1.0631	....	565
	.0605	.0803	.2138	....	1.2520	1.4662		
7	.0605	.0806	.2016	....	1.0080	1.1088	....	550
	.0624	.0833	.2083	.8961	1.3595	....		
8	.0624	.0832	.2080	.8320	1.0400	....	1.5709	585
	.0632	.0839	.2102	.8315	1.1111	1.3331		
9	.0632	.0842	.2106	.8424	1.0530	1.1583	1.4254	580
	.0619	.0823	.2083	....	1.0800	1.2830		
10	.0619	.0825	.2063	....	1.0815	1.1346	1.8100*	637
	.0661	.0884	.2220	.9276	1.1772	1.3775		
	.0661	.0881	.2203	.8812	1.1015	1.2116		

From these experiments I think we may draw the following conclusions :—

That the Modulus of Elasticity depends not only upon the elasticity of the material, but also upon the length of time the load is applied.

That when subjected to loads not exceeding one-sixth of the breaking weight, spruce beams do not take a permanent set.

That even under very small loads, if applied for any length of time, there will be a temporary set.

That knots and knarls in beams loaded at the centre, when not within one-eighth of the span of the centre of the beam, do not materially affect the elasticity under small loads.

That the deflection is very nearly proportional to the load, far beyond the customary limits of strain, and that the Modulus is consequently very nearly constant for all moderate deflections.

That a high Modulus of Elasticity does not always accompany high transverse strength; for, as shown by Table I., piece No. 10, which had the greatest transverse strength, gave next to the lowest value of *E*.

That in spruce beams the upper fibres commence to rupture by compression under about four-fifths of the breaking weight, and the

\* Approximately.

neutral axis is very near the centre of the beam, as shown by the fracture.

That beams which are subjected to severe strains for a long time bend more before breaking than those which are broken in a comparatively short time.

That the Modulus of Elasticity of small spruce beams, of a quality such as is used in the best buildings, may be taken at from 1,600,000 to 1,700,000 lbs., and the Modulus of Rupture at about 11,000 lbs.

The only other experiments on American spruce with which the writer is familiar are those made by Mr. R. G. Hatfield, on small beams, 1.6 feet between supports, and some experiments by Mr. Thomas Laslett, of England, on pieces of Canada spruce 2 inches square and 72 inches between supports.

Mr. Hatfield gives as the average value of the transverse strength of a unit beam, 612 lbs.,\* which would give 11,016 lbs. for the Modulus of Rupture.

From data given by Laslett † we obtain as the value of  $R$ , 9,045 lbs.

The value generally given for the Modulus of Elasticity of spruce is 1,600,000 lbs.

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\* Hatfield's Transverse Strains, Table XLII.

† Timber and Timber Trees, Native and Foreign, by Thomas Laslett, Inspector to the Admiralty, London, 1875.



## XV.

## ANTICIPATION OF THE LISSAJOUS CURVES.

BY JOSEPH LOVERING,

*Hollis Professor in Harvard College.*

Presented January 12, 1881.

IN 1857, Lissajous communicated to the French Academy of Sciences his "*Mémoire sur l'Étude Optique des Mouvements Vibratoires*." \* By attaching a mirror to each of two tuning-forks, and reflecting a pencil of light successively from the two mirrors, the resultant motion of the forks was exhibited on a greatly amplified scale. When the vibrations of the tuning-forks were in parallel planes, and the musical interval between them was not exactly in tune, the consequent beats were manifested to the eye, even after they had become insensible to the ear. When the two motions were in rectangular planes, the extremity of the pencil of light described some one of a group of curves, rising to higher orders as the ratio which expressed the musical interval became less simple. Each of these groups could be easily resolved into eight distinct varieties, each variety depending on a definite difference of phase in the two movements. Inasmuch, however, as there are innumerable differences of phase between any two well-marked limits, there must be an endless series of curves in each group, through which each variety flows gradually into the next. Lissajous studied the subject analytically as well as experimentally, and then applied it to his optical method of tuning notes, especially those of tuning forks, to any required interval. If the vibrations of the forks were true to the precise ratio of this interval, the resultant orbit of the twice-reflected ray would be invariable: and it would be one or another variety in the corresponding group of curves, as the original difference of phase was smaller or larger. If the movements of the two forks did not conform to the exact ratio, the original difference of phase would change with each successive vibration, and the whole group of

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\* *Annales de Chim. et de Phys.*, vol. li. 1857.



curves would be presented in succession. From the rapidity of this succession, the rate at which the phase changed would be known, and hence the degree of imperfection in the assumed interval.

The admiration of physicists was elicited by Lissajous's method of magnifying the mere trembling of a rigid tuning-fork into a visible magnitude; and especially by his optical method of tuning, which, in the hands of even a deaf person, would give better results than were possible to the nicest musical ear. Of these groups of beautiful curves, a few, as the circle, ellipse, parabola, and lemniscate, were not unfamiliar to mathematical and physical science. But most of them were supposed to be novel, and have been introduced into later works on Mechanics and Acoustics under the name of the "Lissajous curves." Many modifications have been introduced into the original experiments of Lissajous, either by himself or others. Reeds, driven by a bellows, have been substituted for tuning-forks. A steel rod, with an appropriate cross-section and mounted with a mirror, admits of the two elementary vibrations in rectangular planes. Two vibrating disks, with rectangular slits, which allow the light to pass only at their intersection, answer the same purpose. Sometimes one vibration is given to a small aperture through which the light passes, and the other to a lens which forms its image on a screen or in the eye. Wheatstone produced, in a single reflector, the two rectangular movements by mechanical means. König, and more recently Ritchie, have used mechanism with two mirrors. The tonophant of Ladd consists of a compound rod, flattened in two rectangular planes. Barrett succeeded with a round and bent steel wire.

It appears that in 1844, Professor Blackburn\* of Glasgow experimented with a pendulum, in which the bob was suspended by a Y-shaped cord; the length of the pendulum being *virtually* the total length, or only that of the lower branch, in the two principal planes of vibration. In 1871, Mr. Hubert Airy† noticed the curious curves described by the end of a twig of acacia and of hazel. In pursuing the subject, he finally adopted Blackburn's compound pendulum, and reproduced many of the Lissajous curves; but he makes no allusion either to Lissajous or to Blackburn. Airy calls the orbits he obtained autographic curves, as they were neatly drawn by a pencil or pen, attached to the pendulum. Before and since that time, various machines were contrived for obtaining a permanent record of these

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\* Tait's Dynamics of a Particle, 3d ed. p. 224.

† Nature, vol. iv. pp. 310 and 370.

complex and diversified motions, whether produced by the vibration of elastic bodies or by machinery. Lissajous and Desains, with an apparatus constructed by Froment, scratched the curves upon smoked glass, the style being moved by one vibrating body and the glass by the other. Professor Pickering\* moved a pen and paper in rectangular directions by machinery, and described the curves on a much larger scale. Donkin† contrived a machine for the graphical representation of a number of parallel vibrations; but the most complete apparatus of the kind is Tisley's harmonograph,‡ which can be suited to parallel, perpendicular, or oblique vibrations; and in a great variety of ratios. The motions of the pen and paper are produced by two independent pendulums, delicately mounted and heavily loaded, so as to maintain their vibration for a long time. The ratios can be altered by a change of weight, combined with a change in the length of one of the pendulums. The latter adjustment can be neatly applied, for making or disturbing the exact ratio of the required interval, without stopping the motion of the pendulum.

As far back as 1800, Dr. Young§ experimented upon the variegated path described by a single point of a silvered vibrating cord, illuminated by strong sunlight. In 1827,|| Wheatstone invented the kaleidophone: which was simply a vibrating wire, with a bead at the free end, and short enough to give persistent vision for the orbit. But neither Young nor Wheatstone have given a mathematical analysis of the motions; the exquisite figures they obtained were due, mostly, to the superposition of the higher harmonics, and few of them are identical with the Lissajous curves. In 1832, Edward Sang¶ of Edinburgh developed mathematically the resultant of two rectangular vibrations, having different periods and phases, and illustrated his subject by experiments with round and flat wires, which produced the peculiar Lissajous curves. Drach, who himself, in 1846,\*\* published his theoretical studies on the combination of two circular motions, with their resulting epicyclical curves, states that Perigal devised machinery which traced curves identical with those of Airy, and, therefore, with those of Lissajous. This machine was exhibited, in 1846,

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\* Journal of Franklin Institute, January, 1869.

† Proc. Roy. Soc. London, vol. xxii. (1874), p. 197.

‡ Engineering, vol. xvii. (1874) p. 101.

§ Trans. Roy. Soc., London (1800).

|| Collected Papers.

¶ Edinb. Phil. Jour., vol. xii. (1832) p. 317.

\*\* Phil. Mag., London, vols. xxxiv. pp. 448, 449 and xxxv. (1849-50).

at a scientific *soirée* in the house of Lord Northampton. Three volumes of Perigal's kinematic curves are preserved in the archives of the Royal Society of London, of the Royal Astronomical Society, and of the Royal Society.

But all these anticipations of the Lissajous curves, theoretical and experimental, are antedated by two publications which appeared at Boston in 1815.\* In this year Professor Dean, of Burlington, Vermont, published a curious memoir on the "Motions of the Earth as seen from the Moon." It is well known that the time of the moon's rotation on its axis is equal to the time of its revolution in its orbit. The result of this equality (whether regarded as a mere coincidence or the effect of gravitation) is seen in the fact that the same side of the moon is always turned towards the earth. This statement would be literally true if the moon's motions of rotation and revolution were in parallel planes, and the *momentary* velocities as well as the *average* velocities were always equal. But the plane of the moon's equator is inclined to the plane of the moon's orbit at an angle of  $6^{\circ} 39'$ ; so that an observer on the earth, at one time, overlooks the north pole of the moon to the extent of  $6^{\circ} 39'$ , and about a fortnight later the south pole. Moreover, the velocity of rotation is uniform, but the velocity of revolution is unequal in different parts of the elliptical orbit. Therefore, although the whole periods are the same for both motions, the moon at perigee revolves faster than it rotates, and at apogee it rotates faster than it revolves. Hence, in the course of one revolution, an observer on the earth overlooks the eastern or the western edge of the moon to the extent of  $6^{\circ} 18'$  each way, or the greatest equation of the centre of the moon's orbit. These effects are familiar to astronomers under the name of the moon's librations, which enable them to see every month four sevenths of the moon's surface, though the remaining three sevenths are forever hidden from view.

Professor Dean investigates the influence of these peculiarities in the moon's motion on the position of the earth as seen by a lunar observer. If the two motions of the moon were equal and parallel, without any qualification, the earth would always occupy the same place in the lunar firmament. If the observer were happily situated at the centre of the moon's visible disk, the earth would always be in his zenith. But the inclination of the planes of the moon's equator and orbit will make the earth appear to oscillate over a north and

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\* Memoirs of Amer. Acad. of Arts and Sciences, 1st series, vol. iii. p. 241 (1815).

south line,  $13^{\circ} 18'$  in length. The want of uniformity in the velocity of the moon's revolution will produce an easterly and westerly oscillation in the earth's position, to the extent of  $12^{\circ} 36'$ . Nature here offers an astronomical example, on a grand scale, of two rectangular vibrations of nearly equal amplitude. It is the case of a unison, but a unison not exactly in tune. For the monthly period which governs both motions is not measured in exactly the same way for both. The period of the first oscillation is the time in which the moon revolves from a node to the same node again. The period of the second oscillation is the time occupied by the moon in going from perigee to perigee again. If the node and the perigee were fixed points, the two periods would be equal. But the node and perigee, in the mean while, are both moving; the former about  $1\frac{1}{2}^{\circ}$  to the west, and the latter about  $3^{\circ}$  to the east. Hence the periods of the two oscillations will be in the ratio of about  $358\frac{1}{2}$  to 363, or of  $79\frac{1}{2}$  to  $80\frac{1}{2}$ . In the course of eighty oscillations, the north and south one would gain one whole oscillation upon the other; and once, in about every six years, the earth, as seen from the moon, would appear to describe upon the sky all the varieties in Lissajous's first group of orbits. To illustrate the subject, Dean devised the compound pendulum, supposed to have been introduced into science twenty-nine years afterwards by Blackburn. The total length of the cord was forty inches and that of the single branch thirty-nine inches. With these proportions, he realized the case of a unison at fault to the required degree; and he had the satisfaction of seeing the suspended bob move over, in the period of eighty vibrations, the complete series of paths pertaining to all the changes of phase of an imperfect unison.

In the same year, an elaborate memoir was published by Dr. Nathaniel Bowditch,\* "On the Motion of a Pendulum suspended from two Points," which begins with this paragraph,—"The remarkable variety of motions in a pendulum suspended from two points, in the curious experiment in Professor Dean's paper on the apparent motion of the earth, as viewed from the moon, induced me to examine the theory of such motions, and I have found the fluents of the fundamental equations, where the arcs of oscillation are small, which is the case usually considered in simple pendulums. Some of the most important results of this calculation are contained in the following articles."

Dr. Bowditch found that the equation which expressed the path described by the end of the pendulum was, in the general case, tran-

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\* *Memoirs Amer. Acad.*, 1st series, vol. iii. p. 413.

scendental, but became algebraical when the periods of the component motions were in some simple ratio, either exactly or approximately. He developed in detail: 1. The unison; 2. The octave; 3. The twelfth; 4. The double octave: and all of them whether perfect or out of tune. His investigation had no reference to acoustics; and he describes these cases by their ratios, and not by the musical intervals which these ratios may represent. He adds that similar results would be obtained if the longer period, divided by the shorter, were expressed by any whole number, either exactly or approximately. Such ratios as 2:3 or 3:4, etc., did not come within the scope of his paper. Dr. Bowditch obtains the equations for the few cases which he specially examines, and finds that for the unison the path is expressed by an equation of the first or the second order; for the octave, by an equation of the second or fourth order; for the ratio 1:3, by an equation of the third or the sixth order; and for the double octave, by an equation of the fourth or eighth order: in each case the equation being of a lower order when the difference of phase in the two movements is zero or  $180^\circ$ .

Dr. Bowditch adds: "I made a few experiments in order to compare the preceding theory with observation." In his first experiment, the two points of suspension were 4.75 inches apart, the single branch of the thread was 46.5 inches, and the *vertical* height of the double branch only .65 of an inch. Therefore the two movements were more nearly in unison than in Professor Dean's experiment. A ball of lead about half an inch in diameter hung at the bottom. By calculation one movement would gain a whole vibration upon the other in 286 vibrations of the more rapid movement: by experiment the number came out 282. In another experiment, the two points of suspension were 69 inches asunder: the single branch of the pendulum was 21.9 inches, and the vertical height of the double branch 64.4 inches. A ball of lead  $1\frac{3}{4}$  inches in diameter was attached. In this case the two movements differed in period by the interval of an octave, imperfect to the extent of one vibration in sixty-seven of the slower movement; and experiment confirmed this conclusion, the whole cycle of orbits being completed in that time. In regard to the two other ratios, Dr. Bowditch says: "A few rough experiments were, however, made in these cases, and the results appeared to be sufficiently conformable to the theory." This kind of experiment is not suited to such ratios as 1:3 and 1:4. For in these cases the single branch of the cord is only one ninth and one sixteenth of the total length, and the amplitude of its vibration comparatively small.

I have now traced the mathematical analysis and the experimental illustration of the Lissajous curves from France to Great Britain, and thence, across the ocean, to their home in Salem, Massachusetts. The so-called Lissajous curves are the Bowditch curves, except so far as the earth itself had been experimenting upon one set of them for thousands of years. They will continue, probably, to be called the Lissajous curves. But their history should be known, and will be known; though it is not necessary for the reputation of the self-taught mathematician, Dr. Nathaniel Bowditch. The author of the "Practical Navigator," and the translator of Laplace's "Mécanique Céleste," with its rich commentary, has secured a place in the world of commerce and in the world of science to which nothing need be or can be added.

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#### EXPLANATION OF THE PLATE.

Figure 1. Professor Dean's diagram, illustrating his pendulum.

Figures 2, 3, 4, and 5. Dr. Bowditch's diagrams to show the orbits in an imperfect unison.

Figure 6. Dr. Bowditch's diagram to illustrate the progressive changes in the orbit.

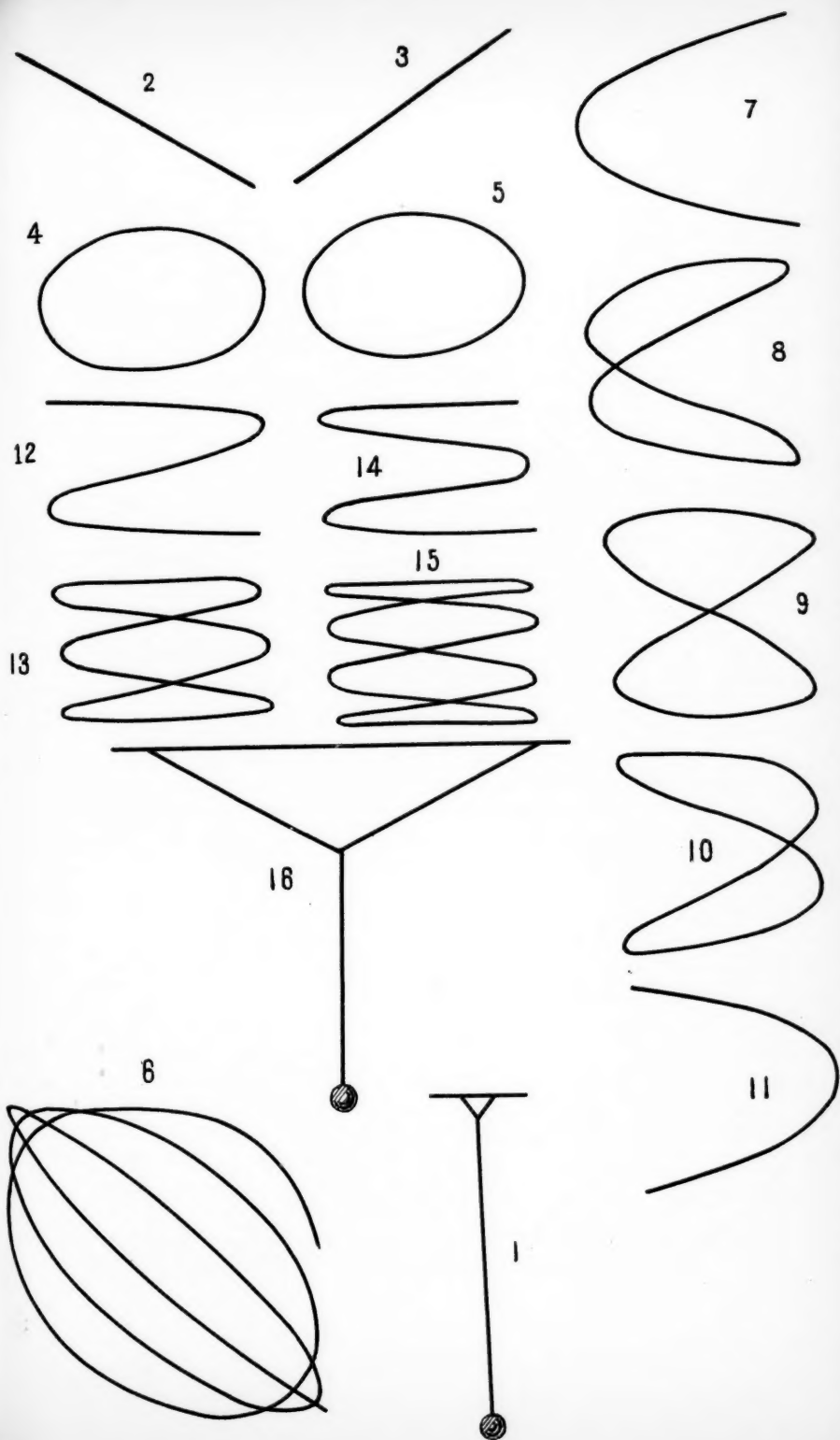
Figures 7, 8, 9, 10 and 11. Dr. Bowditch's diagram to show the orbits in an imperfect octave.

Figures 12 and 13. Dr. Bowditch's diagram for special differences of phase in the ratio, 1:3.

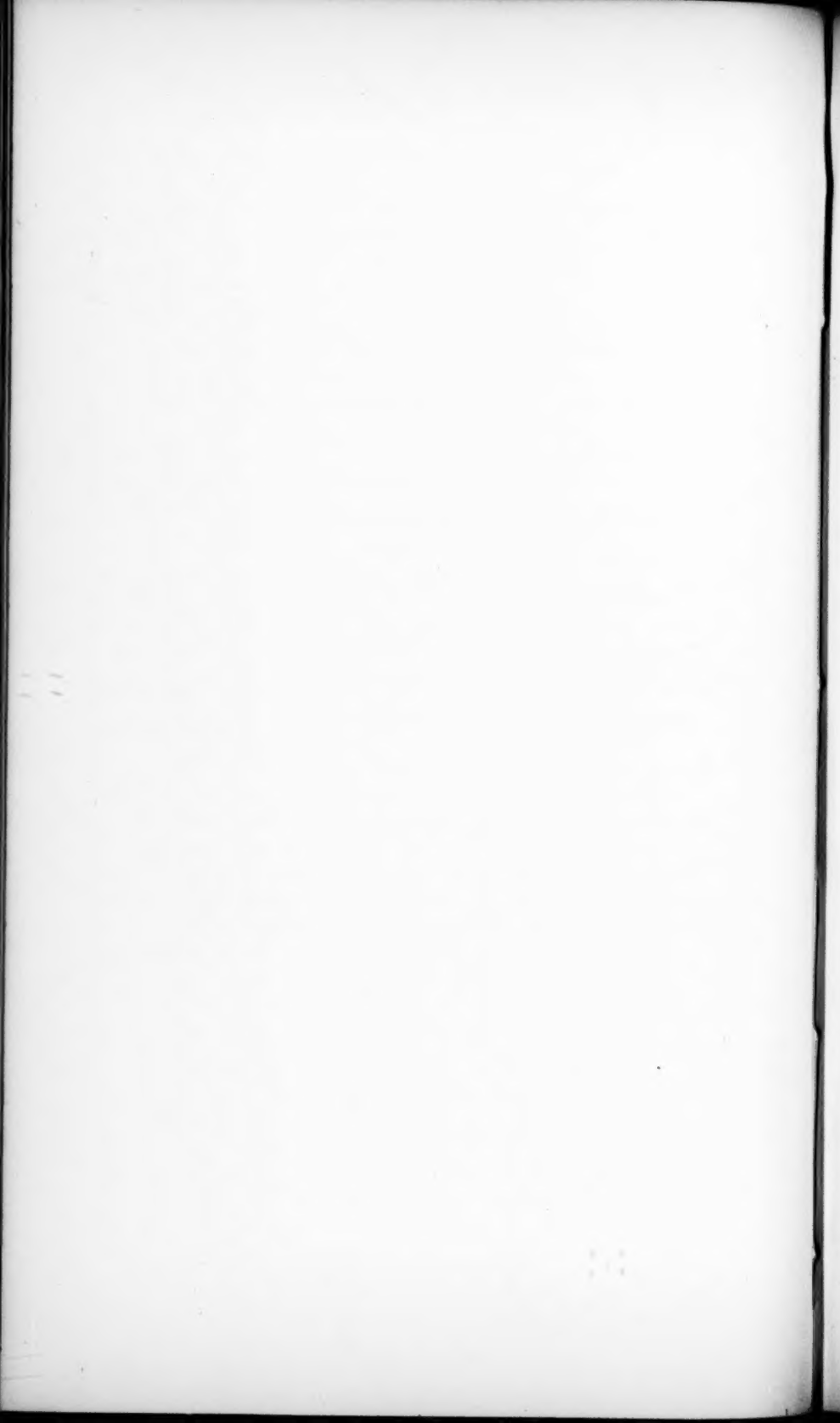
Figures 14 and 15. The same when the ratio was 1:4.

Figure 16. General diagram of Dr. Bowditch's pendulum.

All these figures are exact copies of those published in the Plates of the Academy, vol. iii. 1st series, 1815.







## XVI.

## OBSERVATIONS ON JUPITER.

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IN the year 1876, a series of observations on the planets Mercury, Venus, Mars, Jupiter, and Saturn was undertaken with the intention of following each one of these bodies for as many years as necessary to study them on every point of their orbit, in order to arrive at a better knowledge of their physical constitution and meteorology. The plan then formed was to make at least one observation and a drawing of each planet on every favorable day, whenever the object would be so situated that it could be advantageously observed. So far, this plan has been carried out, and over 1,500 observations, accompanied by 1,000 drawings, have been made.

It is my purpose in this paper to make as brief a statement as possible of those portions of my observations pertaining to the rotation of Jupiter, and the great red spot which made its appearance upon its surface in the year 1878; reserving the rest for publication whenever means shall be found for printing the plates in a suitable manner.

The facts here recorded were selected from the 591 observations and 567 drawings of the series made during the last five years.

The year 1876, the first of my regular and systematic observations of Jupiter, was one of extraordinary disturbance, and nothing approaching it has since been witnessed. The changes were so rapid that, save in one case, no spots or markings could be recognized the day, nay, sometimes even the hour, after they had been observed. Since that time, the surface of the planet has been remarkably quiet, only an occasional change taking place. During the last four years some of the markings have been very persistent, and remained in sight for years, with but very little apparent change.

## MARK A.

In one case only, as has been said above, was a spot recognized in 1876. This object, first seen on May 19, was recognized on May 21,

after having accomplished five rotations, the mean of which equals  $9^h 47^m 0^s$ . The position of this spot was in the northern part of the equatorial belt, extending as far as its border on that side. For convenience we will call this marking A: the other markings to be described will be similarly designated by a letter of the alphabet.

#### MARK B.

In contrast with the usual behavior of the spots seen on the surface of Jupiter in years of calm, and also to show how much these spots are to be relied upon to determine the period of rotation of the planet, I will give a brief account of an observation made in 1876, from which an idea can be formed of the rapidity with which changes sometimes take place on Jupiter, and of the swiftness which sometimes animates these spots.

On May 25, Jupiter was observed and a drawing made at  $8^h 37^m$ . At this time, and at least five minutes later, nothing unusual or remarkable was to be seen on the planet. At  $9^h 4^m$ , however, an angular marking resting on the outside border of the equatorial belt, on its south side, was visible near the east limb. This mark advanced rapidly towards the centre of the disk, which it had passed at  $9^h 32^m$ , when a third drawing was made. At  $9^h 50^m$  the angular marking had reached the western limb, having then crossed the disk of Jupiter from east to west in less than an hour's time.

The angular mark of which the motion has just been described was formed by an oblique dark band, resting on its preceding side on the upper band, forming the southern margin of the equatorial belt. As the angular mark advanced on the disk, the space behind it enlarged considerably, the upper band limiting it southwards, keeping the same obliquity with the equatorial belt as far as it could be seen on the east limb. At  $9^h 32^m$  the oblique band on the east limb had a latitude of  $50^\circ$  south. After the angular mark had crossed the western limb, it continued its tremendous onward motion, as could be seen by the constantly increasing latitude of the upper band on the west limb, and at  $10^h 20^m$  this upper band was parallel with the southern border of the equatorial belt. The space then comprised between this upper band and the southern margin of the equatorial belt was equal to  $35^\circ$ , and was about twice as broad as the latter belt before the disturbance occurred. This space appeared tinted with a delicate pink color, intermingled with white cumulus-like spots resembling exactly those usually seen on the equatorial belt. When the upper band reached

parallelism with the equatorial belt, at  $10^h 20^m$ , the pink color formed a wide belt extending from  $10^\circ$  of north latitude to  $45^\circ$  of south latitude, being therefore  $55^\circ$  in breadth.

Not only that zone of Jupiter was in commotion, but the whole of the southern hemisphere participated in it up to the pole, as proved by the total change of the markings, and the swelling of all the bands to higher southern latitudes on their following side. One of the bands, which on the western limb was at  $30^\circ$  south, was swollen to the south pole on its following extremity. It is to be noted that, in this great disturbance, the bands, although enormously swollen on the following side, still maintained the same distance from each other; each one keeping pace with the other, and following it in all its sinuosities, the effect being apparently the same as if a wedge had been driven from east to west between the upper border of the equatorial belt and the oblique band described. On many occasions in 1876, this continuous parallelism between the different bands in the midst of disturbances was observed, as if the force causing the disturbance had been moving from east to west, between the vapory envelope of Jupiter, and pushing it aside in its passage, as a ship parts the waves of the ocean.

On the following day no traces of this great storm appeared; but everything seemed quiet, the equatorial belt having resumed the same appearance it had on the 25th, before the commotion occurred.

If we determine the period of rotation of Jupiter from the observations of this angular marking, which will be called B, it is found to be very nearly two hours, a period which is very far from agreeing with that found by the observations on the mark A above described, and the adopted period until lately, viz.  $9^h 55^m 41^s$ . The last two periods may be called the periods of calm, while the first may be called the period of disturbance.

#### MARK C.

In 1876 the observations on Jupiter were discontinued after Oct. 19, and resumed after conjunction, on April 11, 1877. On that day a very characteristic mark, resembling a step seen in profile, was observed on the southern border of the equatorial belt, which at one point was deflected at a right angle, the western portion of the belt, or preceding side, being narrower than the eastern or following side.

This step-like marking, which will be called C, was a new form, which had not once been seen in 1876. It remained visible through-

out the year 1877 as late as Dec. 2, when the observations were abandoned, owing to the proximity of Jupiter to the Sun. In 1878, only a few scattered observations were made from the 10th of February to the end of August, the work being resumed regularly in September only. On the 10th, a step-like marking, resembling that observed the year before, was seen on the southern border of the equatorial belt, apparently at the same place which that mark occupied. It was probably the same object, as seems to result from the calculation of its period of rotation, and from its position in regard to the mark D, which will be next described.

In the following table are given the dates and times of the passages of the mark C on the central meridian. Similar tables will be given for the other markings described in this paper. The passages of the markings or spots on the central meridian have not been obtained by micrometrical measurements, but are simple eye estimations. This, of course, renders them liable to errors, which cannot, however, exceed two minutes in most cases, I think.

The passages tabulated have not all been obtained by direct telescopic observations in the way described just now, about one third only having thus been observed. The others were obtained afterwards from the drawings themselves, the marking being reduced to the meridian from its position on the drawing, either east or west of the centre. These passages, of course, are liable to still larger errors than the former, the chances for error becoming greater as the distance from the centre increases. For this reason, the position of the markings at the time of observation, that is to say, their distance in time east or west of the central meridian, is given after each passage thus obtained; the symbol  $+$  indicating that it had passed the meridian, and was west of it by the time given when the observation was made; and the symbol  $-$  indicating that it was east of it, and had not yet reached the meridian, which it would cross only after the time given had elapsed. The passages on the central meridian which were obtained by direct telescopic observation in the manner above described are distinguished from the others by the words "On meridian" placed in the third column.

The time given throughout this paper is the local time, or Cambridge mean time. The above remarks apply to all observations and markings tabulated, as well as the arrangement here adopted.

On July 25 some changes were observed in the mark C, also on Sept. 16 and 21, when the changes were most striking; possibly a jump may be found on these dates.

		h. m.	h. m.		h. m.	h. m.
1877, April 11		15 50	On meridian.	1877, Sept. 12	6 5	+ 1 0
" May 8		14 10	+ 1 8	" " 13	8 87	- 1 40
" " 22		14 45	+ 0 30	" " 16	6 40	+ 0 10
" July 3		9 22	+ 0 15	" " 21	6 40	+ 0 30
" " 22		10 3	+ 0 43	" " 30	7 35	- 1 10
" " 25		15 45	+ 0 50	" Oct. 10	6 2	- 0 12
" Aug. 6		16 17	+ 0 5	" " 15	5 0	- 0 30
" " 8		17 37	+ 0 7	" " 17	6 50	On meridian.
" " 10		19 46	- 1 0	" " 27	5 30	On meridian.
" " 11		15 49	+ 1 30	" Nov. 3	5 52	- 0 10
" " 18		6 50	+ 1 30	" " 15	6 30	- 1 05
" " 22		10 45	- 0 30	" " 20	4 55	+ 0 25
" " 30		7 10	On meridian.	" Dec. 2	4 58	On meridian.
" Sept. 4		6 12	+ 0 50	1878, Sept. 10	6 12	+ 0 48
" " 11		7 5	On meridian.			

The mean period of rotation given by mark C, as obtained from 567 rotations, from April 11 to Dec. 2, equals  $35,740.5^s$  or  $9^h 55^m 40.5^s$ . By taking the whole period of observations from April 11, 1877, to Sept. 10, 1878, we have 1,249 rotations, the mean of which is over four seconds and a half less, or  $9^h 55^m 35.9^s$ .

#### MARK D.

Another permanent and characteristic marking was also observed in 1877 on the southern border of the equatorial belt, following the step-like mark C, above described, at a distance of about 80 or 85 degrees. This mark was of an angular form produced on the preceding side by the straight border line of the broader part of the equatorial belt, and the sloping curved line joining the broadest to the narrowest portion of this belt on the following side.

This angular mark, observed first on April 14, continued visible throughout the year 1877, and was seen as late as Nov. 6, when the observations were discontinued, owing to the proximity of Jupiter to the Sun. It was found again in 1878, on Sept. 8, when I resumed my regular observations; and it continued to be seen through that year, and also in 1879, until the end of August, when it slowly disappeared, the equatorial belt then resuming its usual uniform width throughout.

It is impossible from my observations to know the exact time of the first appearance of this mark, but it is certain that it was not once seen in 1876 from the end of March to the 19th of October, although the planet was observed and drawn one hundred and twenty-five times during this interval.

Singularly enough I find a similar mark on the southern border of the equatorial belt, exactly represented in a drawing by Mr. Camille Flammarion, made on April 22, 1874, in Paris, and published in "Les Terres du Ciel," fig. 174, page 479. But unfortunately the time is not given; and, thus far, I have been unable to obtain it from its author. By assuming that the observation was made at eight o'clock, Paris mean time, and adopting the period of rotation of the similar mark observed by me in 1877-78, it is found that Mr. Flammarion's marking comes within fifty minutes of time of the place it should have occupied had it been the same object as that observed by me. Notwithstanding its disappearance in 1876, it does not seem unlikely that this is the same marking I observed three years later, or at least a recurrence of the same form at the same place, as it might be conceived to happen sometimes by the renewal of the same local causes.

Below is a table giving the dates and times of the passages of marking D on the central meridian.

		h. m.	h. m.			h. m.	h. m.
1877, April 14		15 55	+ 0 35	1877, Sept. 2		6 50	On meridian.
" " 26		16 15	On meridian.	" " 4		8 35	- 1 0
" May 3		17 5	- 0 35	" " 9		7 15	+ 0 25
" " 6		14 20	+ 1 0	" " 14		6 25	+ 0 45
" " 8		16 8	- 0 30	" " 26		6 0	+ 1 15
" " 25		14 32	+ 0 45	" " 29		5 20	+ 1 10
" " 27		16 35	- 0 30	" Oct. 6		4 28	+ 1 0
" " 30		13 55	+ 0 30	" " 13		5 3	+ 0 42
" June 11		13 10	+ 1 20	" " 30		4 20	+ 1 20
" " 18		14 22	On meridian.	" Nov. 1		5 47	- 0 12
" " 20		13 40	+ 0 40	" " 4		3 50	+ 1 30
" " 23		13 0	+ 1 25	" " 6		4 47	+ 0 33
" " 24		9 10	On meridian.	1878, Sept. 8		5 35	+ 1 25
" " 25		15 2	- 0 42	" " 20		7 5	+ 0 30
" " 29		8 3	+ 0 47	" " 25		6 10	+ 0 20
" July 4		7 15	+ 1 10	" " 30		5 0	+ 1 15
" " 6		9 12	- 0 30	" Oct. 2		5 30	+ 0 50
" " 15		11 23	+ 0 50	" Nov. 12		5 50	+ 1 0
" " 18		9 0	On meridian.	" " 24		6 10	On meridian.
" " 23		7 58	+ 1 12	" " 29		4 55	+ 0 20
" Aug. 4		16 47	On meridian.	" Dec. 16		3 55	+ 1 0
" " 6		18 24	On meridian.	" " 23		4 52	+ 0 30
" " 11		18 4	- 0 45	" " 28		3 55	+ 1 0
" " 16		7 35	On meridian.	1879, May 25		15 45	+ 0 30
" " 23		8 20	On meridian.	" July 24		15 12	+ 0 23
" " 26		5 40	+ 0 50	" Aug. 21		8 5	+ 1 10
" " 28		7 20	On meridian.				

On June 20, 1877, the mark D had its form greatly altered, and



then appeared a very different object, but the change was only temporary, as on the 23d it had resumed its former appearance. However, it is probable that some irregularity will be found on that date, and a jump may be noticed.

Between the 14th and 26th of September, 1877, the angular mark D was not seen, although ten observations and drawings were made during that interval. From calculation of the period of this mark, it is found that it should have been on the disk on the 16th, 19th, and 23d, at the time the observations were made. On the 16th, it should have been  $1^h 16^m$  east of the centre; on the 19th,  $2^h 9^m$  west, and on the 23d,  $1^h 3^m$  east of it. If the marking had been visible, it certainly could not have escaped my observation on the 16th and 23d, when it was less than  $40^\circ$  from the centre, especially as the sight was very good at the time the observations were made. On the 19th, it might have passed unnoticed, as it must have been quite close to the limb and considerably foreshortened.

At the time the disappearance of this mark occurred, great changes were seen to be going on, in and about the equatorial belt, from which the disappearance probably resulted.

On the 26th, as already said, the mark was seen again, at the same place, and with precisely the same characteristic form it had from the beginning of my observations.

Again, from Nov. 6 to Dec. 9 of the same year, the same angular marking was not once seen, although the planet was observed and drawn thirteen times during this interval. Calculation showed that it should have been visible in November, on the 13th,  $37^m$  east; on the 15th,  $1^h 52^m$  east; on the 18th,  $26^m$  west; on the 20th,  $1^h 9^m$  east; and on the 30th,  $15^m$  west of the central meridian; while in December it should also have been on the disk on the 2d,  $1^h 34^m$  east, and on the 3d,  $2^h 19^m$  west of the centre. But not the slightest traces of it were detected, although looked for; not even on the 13th, 18th, and 30th of November, when it should have been close to the central meridian.

On Nov. 13th, when this mark should have been near the centre, it was found that, at the very place it should have occupied, the southern margin of the equatorial belt was wavy, irregular, and somewhat swollen, but nothing looking like the familiar object so often observed was visible.

After Dec. 9, 1877, the observations were discontinued, Jupiter being too near the Sun to be observed with advantage, and were not regularly resumed after conjunction until Sept. 6, 1878.

Although scattered observations were made on Feb. 12 and 13, March 7 and 15, May 27, and June 13, no angular marking was seen. On Sept. 8, however, the same mark reappeared, and remained visible until the end of August, 1879.

On Sept. 10, the angular marking seen on the 8th should have been in sight, and within a few degrees of the central meridian, had it followed its regular proper motion; but it was not found on the disk. West of the meridian, however, the step-like mark C was visible, thus indicating that the angular mark was in the east very close to the limb. In order to have been at that place, the marks C and D, and perhaps the whole equatorial belt, must have moved backwards, and retrograded in these two days some  $75^{\circ}$  or  $80^{\circ}$ .

On the 25th of September, the great red spot was seen following very closely the angular mark D, and both kept their relative distance until the disappearance of the latter in the following year.

From the fact that this mark disappeared and re-appeared several times, it may be supposed that it was hidden from sight by opaque clouds or vapors floating high above it, and thus concealing it for some time. But the great jump observed between the 8th and 10th of September, 1878, shows that these markings, having no fixity at all, are liable to be transported to great distances by the forces at work on Jupiter, or to be destroyed and generated again afterwards; only, in the last case, it would seem singular that they should reappear in the same form.

#### THE GREAT RED SPOT, OR MARK E.

This curious and remarkable spot was seen by me for the first time on Sept. 25, 1878. Since then, I have drawn it one hundred and thirteen times in various positions upon the disk.

In the following table will be found the dates and times of the passages of the centre or of either of the extremities of this spot on the central meridian.

It would have been desirable to give in this paper the longitudes of the marks and spots at the time of their passage of the central meridian, as thus their proper motion and irregularities might have been easily ascertained. But as I had not an ephemeris at hand, giving the time when the assumed first meridian traversed the middle of the disk, of an earlier date than that of Sept. 18, 1880, I have been obliged to give the spots observed before that date without their corresponding longitudes. Those observed later, however, have their longitudes given in the last column, in which the daily rate of rotation is assumed to be  $870.60^{\circ}$ .

			h.	m.	
1878	Sept.	25	6	55	Centre on meridian.
"	"	30	6	5	" " "
"	Oct.	2	7	5	" " "
"	Nov.	12	6	50	Following end on meridian.
"	"	24	6	10	Preceding " "
"	"	29	5	15	" " "
"	Dec.	16	4	40	Centre on meridian.
"	"	23	5	33	" " "
"	"	28	4	45	" " "
1879	April	7	17	25	" " "
"	May	25	16	15	Preceding end on meridian.
"	July	5	16	0	Following " "
"	"	12	15	45	Preceding " "
"	"	24	15	30	" " "
"	"	29	15	45	Following " "
"	Aug.	12	16	0	Preceding " "
"	"	21	9	0	Centre on meridian.
"	Dec.	7	7	20	Preceding end on meridian.
"	"	12	6	26	" " "
"	"	29	5	25	" " "
1880	Jan.	3	5	11	Centre on meridian.
"	"	5	6	20	Preceding end on meridian.
"	"	8	4	45	Following " "
"	"	10	5	25	Preceding " "
"	"	24	7	4	" " "
"	"	29	6	8	" " "
"	Feb.	22	6	6	" " "
"	Aug.	9	10	56	Centre on meridian.
"	"	26	9	55	" " "
"	Sept.	12	8	50	" " "
"	"	17	7	56	" " "
				Preceding.	Centre.
1880	Sept.	24	8	39	805 38.4
"	"	26	10	48	. . .
"	"	29	7	44	. . .
"	Oct.	1	9	18	. . .
"	"	6	8	27	. . .
"	"	11	7	34	. . .
"	"	13	8	38	307 44.4
"	"	18	8	16	. . .
"	"	23	7	23	. . .
"	"	28	7	6	. . .
"	Nov.	1	9	52	. . .
"	"	2	5	40	. . .
"	"	8	10	35	. . .
"	"	9	6	20	. . .
"	"	16	7	7	. . .
"	"	18	8	47	. . .
					Following.
					824 14.6
					343 37.2
					324 7.2
					323 2.4
					325 51.6
					327 26.4
					327 26.4
					329 16.8
					352 12.0
					335 20.4
					333 39.6
					335 49.2
					332 16.8
					334 53.8
					336 36.0

				Preceding.	Centre.	Following.
1880	Nov.	21	6 16	. . .	337 1 <sup>o</sup> / <sub>2</sub>	
"	"	23	7 51	. . .	335 34.8	
"	Dec.	3	6 7	. . .	338 9.6	
"	"	7	9 29	. . .	342 18.0	
"	"	8	5 19	. . .	341 38.4	
"	"	15	6 4	. . .	342 18.0	
"	"	20	5 11	. . .	342 36.0	
"	"	27	5 35	330 21.6		
1881	Jan.	1	5 12	. . .	348 32.4	
"	"	8	5 55	. . .	347 24.0	
"	"	10	8 10	. . .	. . .	12 18 <sup>o</sup> / <sub>0</sub>
"	"	20	5 52	. . .	350 20.4	
"	Feb.	13	5 50	. . .	0 32.4	
"	"	15	5 4	343 26.4		

By comparing the time of the passages of the red spot on the meridian, given in the first part of the above table, with that given by Mr. A. Marth in the *Monthly Notices*, Vol. XL., No. 8, p. 496, a discrepancy will be found in the time of passage of Sept. 30, Oct. 2, and Dec. 16. I am unaware how this occurred, possibly through an error of mine; but the time should be corrected, that here recorded being right.

I have shown elsewhere \* that the red spot must have disappeared in 1878, in the same manner as did the angular mark D in 1877. This spot, seen by different observers in July, August, and September, was not seen by me on Sept. 20; although, at the time my observation was made, it should have been very near the centre of the disk, and consequently in the best position to be observed. The very place where the red spot was seen five days later, was occupied by a dark irregular, gray band, commencing near the mark D, and extending east as far as the limb. As the sight was good at the time this observation was made, it cannot be supposed for a moment that it escaped my notice. If it had been there, it must certainly have been seen.

At the time of this observation, the red spot might have been concealed by the dark, irregular band already described, or it might have closed up, as the great variations observed in its size and form during the first year after its appearance would seem to suggest. At first the changes of form of the red spot were great and very frequent, and slowly and gradually it acquired the regular and comparatively steady shape it has shown for over a year.

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\* "On the Recurrence of some of the Markings on Jupiter." *The Observatory*, No. 24, April, 1879, p. 411.

When first seen on Sept. 25, 1878, it appeared as a long and narrow form, with a slender, sharp point on its preceding side. The time of the passage of this spot on the meridian, from its preceding to its following extremity, was on that day  $1^h 18^m$ . It retained this form more or less exactly for a few days, but on Oct. 2 it had considerably extended longitudinally, the narrow parallelogrammic form of its following side being prolonged on the preceding end by a very slender and acute point; the whole spot occupying apparently one half the diameter of the disk, and its passage over the meridian, from end to end, being  $2^h 15^m$ .

On Oct. 5 and 17 it was considerably shortened, and on Nov. 12 it was almost oval, with its preceding end pointed. On the contrary, on Nov. 24 its preceding end was cut square, while the following was sharply pointed. On Nov. 29, the preceding end was rounded, while the following was obliquely cut.

On Dec. 16, the form of the red spot was found completely changed, it having two large protuberant masses projecting from its northern margin. One, the larger, was near the following end; the other, smaller, near the preceding end, which was pointed. On Dec. 23, the spot had somewhat diminished in size, and had three protuberances on its northern border, instead of two; but they were a little smaller than those of the 16th. The major axis of the red spot, which, so far, had been parallel to the equatorial belt, was on that day considerably tilted, and inclined to it  $20^\circ$  or  $25^\circ$ , its preceding end being the nearest to the equator. On Dec. 28 and 30, the spot had enlarged considerably, keeping, however, about the same irregular shape, except that it was more pointed on the preceding side, and that the three projections on its northern side were larger. The axis-major of the spot had then resumed its parallelism with the equatorial belt.

On April 7, 1879, the red spot appeared elliptical, although very little elongated; while on May 25 its form was that of a very extended narrow parallelogram having both ends slightly rounded. On July 5, it was oval in shape, or rather egg-form, its preceding end being much wider than the following.

Between this last date and the middle of August, it was constantly changing, but the changes were very slight. On Aug. 21, its preceding end was forked or swallow-tailed, while the following was pointed. On Aug. 28, it had a regular and beautiful oval form. On Dec. 8, it appeared narrower and more extended longitudinally, its delicate color having somewhat lost its purity.

About the beginning of January, 1880, the red spot began to assume the regular oval shape which it has, with but very slight modifications, since retained. These modifications of form consisted principally in that one of its ends appeared narrower, giving it therefore an egg-shape, as that observed on the 1st of November. Its northern margin has also frequently been observed to be deformed, appearing jagged and indented, principally on Aug. 26, Sept. 29, and Dec. 10 of last year. The serrations, projecting on the red spot, sometimes appeared as bright nodules, as if the narrow band separating the red spot from the equatorial belt had been composed at these times of brilliant cumulus-like forms having a higher level than the spot itself.

Although comparatively steady now, the red spot varies almost from day to day in length, as well as in breadth; but most of the time the variations are so slight that the greatest attention is required to notice them, and for most observers it is only once in a while that they become apparent.

The color of the red spot is also subject to some variations, but usually they are slight; and, as these phenomena are more delicate than mere changes of form, it usually requires an expert and trained eye to see them. Apart from the changes in the intensity of its color, which are quite frequent, the variations of color which came under my notice are few, the greatest being, as stated above, when the clear red color of the spot lost its purity, and became muddy and *lie-de-vin* color. Most of the time, the variations in the intensity of the red spot could be attributed to the state of our atmosphere, but sometimes, as in the above case, they seemed to be real, as the pink color of the equatorial belt was not affected, as it would have been if the cause were atmospherical. It will be shown below that sometimes, also, the pink color of the equatorial belt increases considerably in some parts, while it remains unchanged in others.

Throughout the whole month of November, 1880, I had the persistent impression that there were two small, round, black spots, or specks, on the red spot; one being not far from its preceding end, while the other, behind, was a little to the west of its middle, both appearing to be a little nearer the southern than the northern border. On Nov. 30, I had the satisfaction of finding that my impressions were correct, as I plainly and distinctly saw two small, round spots at the place where I had perceived them so many times before. One of these black specks was observed independently by Mr. Alvan Clark, Jr., on

the night of Jan. 5, 1881, with the twenty-two inch refractor he is now constructing for the Princeton Observatory.

On Nov. 1, 1880, the pink color of the northern portion of the equatorial belt, situated above the black spots G, which will be described below, became very intense, and upon it were seen many small black spots and specks resembling those observed on the red spot on the same day, and throughout the months of November and December of the same year.

The red spot has sometimes appeared surrounded by a white ring, which varied in brightness and width. At times it became very brilliant, and appeared as if mottled over by some cloudy specks. This white ring was especially conspicuous in January, October, and November, 1880. From its appearance and brilliancy, it would seem that this luminous ring is formed by an accumulation of clouds, having a higher level than the surrounding surface, and especially that of the red spot. It might be interesting to watch the transit of the shadow of satellites across the common boundary line separating the red spot from the ring, and see if the shadow is deformed by a change of level. But the delicacy of such an observation would be very great, and probably only large instruments could attempt it. On Aug. 24, 1880, I saw the shadow of Satellite I. passing on the thin, white belt separating the red spot from the equatorial belt, and projecting about one third of its disk on the red spot; but I was unable to detect any distortion of its shape, the sight being poor at the time. On Nov. 1 of the same year, the shadow of Satellite II. was observed in transit on the red spot; nothing unusual in its shape was noticed. The most favorable opportunity for such a delicate observation would be when Jupiter is near its quadratures, and the red spot close to the limb. At such a time, the shadow of a satellite crossing the extremity of the red spot nearest to the limb would be seen under its greatest possible distortion. If there be a change of level between the ring and the red spot, it ought, it seems, to be noticeable under good atmospheric definition, but transits under these conditions must necessarily be very rare.

While treating the subject of the red spot, I should not omit to say that this object has not always been unique. While in the Paris Observatory, on Sept. 18 or 19, 1879, I had an opportunity of observing Jupiter with an excellent refractor of eight or nine inches' aperture made by MM. Henri Brothers. At the moment the observation was made, the great red spot was a little to the east of the middle of the disk. Right above and a little preceding it were two small, roundish



red spots, one larger than the other, each surrounded by a brilliant and narrow white ring. I called the attention of the MM. Henri to this fact, which both easily verified. The color of these two small spots was not that of the equatorial belt, which is of a different shade and much less intense, but precisely the same as that of the great red spot, which they, with their bright ring, resembled in miniature. It will be seen below that the pink color sometimes appears instantly in different parts of the disk, and this even in high latitudes.

Allowing for errors of observation, and taking them into account, it is found that the period of rotation of the red spot is irregular, and varies somewhat on certain days, while on others no variation is perceptible. This shows that the red spot, like all other spots described in this paper, is not fixed on the planet, and changes place under the action of internal or external forces.

The mean period of rotation of this spot seems to have slowly decreased for some time. From the end of September to the end of December, 1878, the mean period of rotation is found to be  $9^h 55^m 43.61^s$ ; from the end of December, 1878, to the beginning of January, 1880, the mean period was  $9^h 55^m 36.85^s$ . But from January, 1880, to February, 1881, it is found to be  $9^h 55^m 38.96^s$ . The mean period of rotation from the whole being approximately  $9^h 55^m 38.57^s$ .

#### MARK F.

Besides the great red spot E, and the markings C and D, which were conspicuous and permanent objects, other spots of shorter duration have also been observed, and their proper motion carefully watched.

One of the most characteristic among them appeared inside the equatorial belt, close to its southern border. It consisted of a very bright, round spot, forming the preceding extremity of one of the white, cloud-like spots which constitute the middle zone of the equatorial belt. This bright object protruded considerably southwards on the rosy background of the equatorial belt, and as far as its southern border, which it seemed sometimes to push out and swell at that point.

This spot, although it very likely existed before, was particularly noted on Nov. 16, 1880, and was watched until it disappeared. By going backward and examining the drawings anterior to that date, it was found that one of the markings, much resembling the mark F, was observed as far back as Aug. 8 of the same year, although it was not so brilliant at that time as it has been since, if it is the same spot. As it is thought to be the same object, I will give

the times of its observed passages on the central meridian, together with those observed after the 16th.

1880.	h. m.	h. m.	° /	1880.	h. m.	h. m.	° /
Aug. 28	9 30	On meridian.		Dec. 7	5 31	On meridian	199 30.0
Oct. 18	7 44	+ 0 32	308 38.4	" 9	6 25	+ 0 27	173 56.4
" 25	6 26	+ 0 40	236 52.8	" 14	4 45	On meridian	145 33.6
Nov. 7	7 17	- 0 30	67 33.6	" 16	5 57	" "	130 8.4
" 16	7 37	- 0 30	352 58.8	" 23	4 58	" "	68 9.6
" 18	8 53	- 0 6	340 12.0	" 30	4 23	+ 0 33	20 27.6
" 21	5 36	+ 0 40	313 1.2				
" 23	6 43	+ 1 8	294 46.8	1881.			
" 25	7 56	On meridian	280 8.4	Jan. 1	5 32	- 0 20	3 10.8
" 27	8 57	+ 0 46	258 18.0	" 15	5 0	+ 0 30	287 24.0
" 30	5 58	+ 1 12	241 51.6	" 17	5 2	+ 0 10	229 51.6
				Feb. 7	5 47	On meridian	175 15.6

It is noted in the observing book, on Dec. 23, that the forward motion of the spot seemed to have decreased. Great irregularities will be found in the motion of this spot, amounting from five to thirteen, and even in one case to twenty-nine degrees in a day. It may be that the mark observed on Jan. 17 was a different object altogether, otherwise a large jump has occurred there.

This mark, which lasted at least from the end of August, 1880, seems now to have disappeared, as no traces of it have been seen for over fifteen days. The mean period of rotation of this mark equals  $9^h 51^m 8.30^s$ .

#### MARK G.

Another very conspicuous spot, or rather a series of spots, was also carefully watched from the end of October to the end of December, after which it disappeared.

On Oct. 28, 1880, great changes occurred in the equatorial belt, especially on its northern half, the white, cloudy forms of the central zone changing their shape. At the same time, the delicate rosy color between the cloudy belt near the northern border of the equatorial zone assumed an intensity of color rarely seen, and almost equal to that of the red spot, although of a different shade. While these changes were going on, a row of five black spots, some of which resembled closely the shadows of satellites in transit, only not quite so black and not so sharp in outline, was observed in the northern hemisphere of the planet, forming part of the gray band nearest to the equatorial belt on that side. The first spot of the series on the preceding side was on the central meridian at the same time that the following end of the red spot crossed this line on the 28th of October.

The gray band on which these black spots were formed underwent very rapid changes, and on the following days new spots, similar to the first, appeared, mostly in pairs, at irregular intervals on the following side of the former, until at least one half of the whole circumference of Jupiter was covered with round black spots, differing but little in size and in depth of tint.

Owing to the formation of these new spots, it was difficult to know with certainty which was the one that had been observed before passing the central meridian, and possibly errors may thus have been made in mistaking one for the other, especially from the 28th of October to the 16th of November.

The following table gives the dates and times of the passages of the preceding spot of the row across the central meridian.

1880.	h. m.	h. m.	° /	1880.	h. m.	h. m.	° /
Oct. 28	7 2	+ 0 8	349 48.0	Nov. 8	7 20	+ 0 40	218 49.2
" 31	13 22	- 0 40	311 49.2	" 10	7 25	+ 1 0	163 30.0
Nov. 1	8 48	+ 0 42	296 56.4	" 17	6 30	+ 0 55	104 56.4

Great irregularities will be found in the apparent motion of this mark, and possibly a different spot may have formed on the preceding side, thus producing a jump. This may have occurred between the 8th and 10th of November, when the apparent motion was at the rate of  $27.5^\circ$ ; i. e. this spot gained  $27.5^\circ$  a day on the red spot. The mean period of rotation of the planet obtained from the observation of 49 rotations of this mark equals  $9^h 47^m 6.10^s$ .

#### MARK H.

On Nov. 19, the fifth or sixth spot from the preceding one became considerably darker and more characteristic than the others, projecting a little outside of the row on the north side. It was separated from the next spot on the following side by a larger interval occupied by a brilliant sort of bridge, strongly resembling some of the brilliant faculae which oftentimes separate sun-spots in activity. This facula-like object, together with a sort of bright ring almost encircling it, gave to that spot and the following one a very peculiar look, and bore a striking resemblance to some of the solar spots, which was very suggestive.

In the beginning of December, some changes occurred in these spots, a long and narrow appendage being added to the preceding one, giving it the appearance of a tail preceding it to the southwest for a distance three or four times its own diameter.

On December 16, the black spots began to enlarge considerably, while at the same time they became diffused on their border and much

less dark than they had been, some of them becoming so pale that they could hardly be distinguished. After a few days these enlarged spots, which had become numerous and encircled the planet, disappeared altogether, leaving in their place a broad belt, having a strong resemblance to the equatorial belt, except that it was only half as wide, and having a central cloudy white band enclosed on each side by a space tinted with the delicate pink color which distinguishes the equatorial zone.

I shall here remark that every time I have observed great changes in the configuration of the markings of the surface of Jupiter, they were accompanied by an increase in the intensity of the rose color of that part of the equatorial belt nearest to the place of disturbance. At the time the black spots above described made their appearance, simultaneously with the increase of intensity of the rosy belt, a slight tinge of red was noticed under the black spots, in the northeast, this tinge occupying a great portion of the area constituting the north polar cap. This pinkish tinge went on increasing somewhat in intensity as well as in extent until Nov. 1, when it culminated, then extending from the first gray band north of the one where the black spots had formed to the north limb. The pink tinge then gradually decreased in intensity and in extent, and was last seen on the 24th of November, after which it was confined to the northern pink belt already described. The pink color of the equatorial belt towards the north seemed under the same influence, since it culminated also in intensity on Nov. 1, after which date it gradually decreased until it resumed the same delicate tint with the other parts.

The formation of this series of black sun-spot-like forms, with their subsequent development into a broad pink-tinted belt, is very instructive, inasmuch as it shows us how the forces creating such belts are acting. This action on Jupiter is not without some suggestive points of resemblance to the action creating the similar openings of the Sun's photosphere, which we call sun-spots. As we know, the sun-spots not only have a tendency to form into groups, the axis of which is parallel to the solar equator, — or, if it is not exactly so, it soon attains this parallelism, — but, again, all the groups of one epoch keep on the same parallel of latitude on each side of the equator. If on the Sun the forces creating the spots should increase and continue for some time with the same intensity as seems to be the case on Jupiter, a continuous belt of spots would surround the Sun, and finally a broad belt would result by the breaking up of the thin walls separating every individual spot. On the Sun, of course, the forces required to produce

such an effect must necessarily be more powerful than on Jupiter, since the photosphere of the Sun is undoubtedly much thicker than the cloudy atmosphere of Jupiter, and of a different nature.

The following table gives the time of the passages on the central meridian of the second spot described, that is, the sun-spot-like mark.

1880.	h. m.	h. m.	°	'	1880.	h. m.	h. m.	°	'
Nov. 19	8 5	— 0 40	103	33.6	Dec. 3	5 52	+ 0 15	329	9.6
" 22	4 34	+ 1 18	67	58.8	" 9	7 34	— 0 42	215	20.4
" 24	5 58	+ 0 17	59	56.4	" 14	5 13	— 0 28	162	21.6
" 26	7 13	— 0 27	46	30.0	" 16	6 21	— 1 6	144	32.4
" 30	8 10	— 1 0	321	3.6					

The apparent motion of this spot is still more irregular than that of the passages of spot G, and varies from  $2.3^{\circ}$  to  $21^{\circ}$  a day; and between Nov. 30 and Dec. 3, the motion was even retrograde at the rate of  $2.7^{\circ}$  a day, which means that during these three days this spot had a longer period of rotation than the red spot has. The mean period of rotation of Jupiter as derived from the observation of this spot is  $9^h 47^m 30.90^s$ .

#### MARK I.

The object to be now considered is the preceding extremity of a remarkable white spot observed towards the end of November, 1880, inside the equatorial belt, near its southern border, and situated at about the same latitude as the mark F above described. On Nov. 26, at  $6^h 46^m$ , this mark was apparently under the following end of the great red spot. After Dec. 10, some changes occurred on and around this spot, and from that time it was lost.

The following are the dates and times of its passages on the centre of the disk.

1880.	h. m.	h. m.	°	'	1880.	h. m.	h. m.	°	'
Nov. 26	6 4	+ 0 42	5	6.0	Dec. 7	8 44	+ 0 45	315	18.0
" 30	8 10	— 1 0	357	3.6	" 8	4 29	+ 0 50	311	38.4
Dec. 3	5 32	+ 0 35	317	9.6	" 10	6 2	On meridian.	308	52.8

The apparent motion of this mark is also irregular, and varies from  $0.5^{\circ}$  to  $13^{\circ}$  a day, the largest apparent motion having occurred between the 30th of November and the 3d of December.

The mean period of rotation of the planet as obtained from the observation of this mark is  $9^h 52^m 52.90^s$ .

## MARK J.

The mark of which the passages on the central meridian are here tabulated is the preceding end of a conspicuous white cloudy form belonging to the southern side of the equatorial belt. This mark occupied very nearly the same parallel of latitude as did the marks F and I, already described. On Nov. 8, at 10<sup>h</sup> 35<sup>m</sup> it was on the central meridian with the centre of the great red spot. After Nov. 18, this mark changed so much that it could no longer be recognized among the other forms of the cloudy belt of the equator.

1880.	h.	m.	h.	m.	°	'	1880.	h.	m.	h.	m.	°	'
Nov. 8	10	35	On meridian.		335	49.2	Nov. 14	4	30	+ 1	25	299	6.0
" 9	5	52	+ 0	28	315	28.8	" 16	5	52	+ 1	15	289	58.8
" 11	7	10	- 0	10	303	57.6	" 18	7	29	+ 1	18	289	48.0

The considerable apparent motion between the 8th and 9th of November must be very nearly correct, as both observations were carefully made, and while the mark was on the central meridian. The jump made on that day was over 20°; after that, the mean forward motion was only about 3° daily.

The mean period of rotation of Jupiter as obtained from this mark would be 9<sup>h</sup> 52<sup>m</sup> 15.0<sup>s</sup>.

## MARK K.

Towards the beginning of October, 1880, the red spot was preceded by a long grayish band, cut sharply and obliquely at its preceding end, and from there extending to within a few degrees of the preceding end of the red spot. As this band was situated only a few degrees more to the south than the red spot, I thought it worth while to study its behavior. After Oct. 13, this band contracted rapidly, both of its extremities either retreating towards each other or dissolving; but after the 25th it expanded again lengthwise until the 31st; and was lost entirely the following day.

The passages here given are those of the preceding extremity of this band.

1880.	h.	m.	h.	m.	°	'	1880.	h.	m.	h.	m.	°	'
Oct. 8	8	57	+ 0	28	252	21.6	Oct. 25	7	6	On meridian.	260	52.8	
"	12	11	25	on meridian	258	21.6	"	31	11	42	+ 1	0	251 49.2
"	15	8	59	"	"	262	12.0						

Contrary to the behavior of all the other markings, the apparent motion of this object, when compared with that of the red spot, was retrograde at first, and direct at last.

The rotation period obtained from this object equals 9<sup>h</sup> 55<sup>m</sup> 22.5<sup>s</sup>.

## MARK L.

Soon after the gray band K, above described, had disappeared, some changes occurred in the markings of that particular region of Jupiter. On Nov. 15, a large oval gray spot, resembling the red spot in size and in shape, made its appearance at the same place which the gray band had occupied. On its southern side this oval spot was edged with a narrow bright border, which made it appear more sharply defined on that side. This oblong spot has been carefully observed, and was lost in the beginning of February.

The following are the dates and times of the passages of the centre of this spot on the central meridian.

1880.	h. m.	h. m.	° /	1881.	h. m.	h. m.	° /
Nov. 15	9 37	- 1 30	275 31.2	Jan. 3	4 15	+ 1 15	255 36.0
" 16	5 32	+ 1 35	277 58.8	" 7	8 5	On meridian.	276 6.6
" 30	6 28	+ 0 42	259 51.6	" 15	4 10	+ 1 20	257 34.0
Dec. 10	4 32	+ 1 30	254 52.8	" 17	6 8	- 0 56	289 27.6
" 17	5 33	On meridian.	265 4.8	" 22	4 37	+ 1 0	246 32.4
" 19	7 0	" "	258 36.6	Feb. 2	4 57	+ 0 40	113 42.0
" 22	4 28	+ 0 36	258 10.8	" 4	6 40	+ 0 55	116 42.0

It is doubtful whether the observation of Feb. 2 relates to the same marking as that last seen on Jan. 22, although the object appeared exactly like it in form and in size. On Jan. 31, at 5<sup>h</sup> 38<sup>m</sup>, a dark oval spot was seen on the east limb; undoubtedly this was the same object seen on the 22d, and no other spot was to be seen towards the west, or at any other place. If the spot observed on Feb. 2 had then existed, it would have been less than 2<sup>h</sup> 30<sup>m</sup> distant from and preceding the first, and therefore visible west of the centre of the disk. The spot observed on the 2d, then, must have been either the old one, having made a jump of 118° in two days, or a new form, which appeared between the 31st of January and the 2d of February. It seems probable that the last supposition is the true one.

The apparent proper motion of the spot K has in general been slow and irregular, being sometimes retrograde. If, however, we take its position when first observed on Nov. 15, and that of Jan. 22, when it was last seen, we have a difference of nearly 29° for its direct motion during this interval.

The rotation of Jupiter derived from the observation of this mark would be 9<sup>h</sup> 55<sup>m</sup> 14.60<sup>s</sup>.

Below is a table giving the approximate period of rotation which we would give to Jupiter if it were determined from the observations of the



spots we have described in this paper. The period of each spot is the mean of the number of rotations during which each one was individually observed.

APPROXIMATE PERIOD OF ROTATION OF THE MARKS OBSERVED, IN THEIR ORDER OF DECREASE.

				Mean period of rotation obtained from		
					h.	m. s.
E	From	Sept. 25, 1878	to Feb. 13, 1881	2108 rotations equal	9	55 38.57
D	"	April 14, 1877	" Aug. 21, 1879	2076	"	" 9 55 36.70
C	"	" 11, 1877	" Sept. 10, 1878	1249	"	" 9 55 35.88
K	"	Oct. 3, 1880	" Oct. 31, 1880	68	"	" 9 55 22.05
L	"	Nov. 15, 1880	" Jan. 22, 1881	164	"	" 9 55 14.60
I	"	" 26, 1880	" Dec. 10, 1880	34	"	" 9 52 52.90
J	"	" 8, 1880	" Nov. 18, 1880	24	"	" 9 52 15.00
F	"	" 16, 1880	" Feb. 7, 1881	202	"	" 9 51 8.30
H	"	" 19, 1880	" Dec. 10, 1880	66	"	" 9 47 30.90
G	"	Oct. 28, 1880	" Nov. 17, 1880	49	"	" 9 47 6.10
A	"	May 19, 1876	" May 21, 1876	5	"	" 9 47 0.00
B	"	" 25, 1876		$\frac{1}{2}$	"	" 2 0 0.00

This table shows conclusively that the different spots and markings studied in this paper did not return to the meridian in the same interval of time, each having a distinct and separate period of rotation, varying from  $9^h 55^m 38^s$  to  $2^h$ . Not only each one had a distinct period of rotation, but, again, it is shown by the other tables that the very same spot had different periods of rotation, varying from day to day, and this sometimes considerably. On some days the spots moved rapidly, and made great jumps forward, while on others they moved slowly, and even seemed to retrograde. For the last ten years I have closely observed Jupiter, and the same phenomena have occurred; therefore the proper motion of the markings of the planet is not an accident. In 1876, as already stated, the changes were much more rapid, and on a larger scale, than they have been since. During that year, not a spot or mark, save in one instance, could be recognized on the following day.

Since no marking which could be taken for reference on the surface of Jupiter is absolutely fixed on the planet, it is impossible to obtain the exact period of rotation of the solid nucleus of this body; and it is therefore probable, if not absolutely certain, that no one has yet succeeded in obtaining it. Unless some great changes occur in the constitution of the planet, it is not likely that astronomers are soon to obtain that exact period. The period of rotation which we obtain now is the period of clouds, similar in appearance to those of our earth, floating in a dense atmosphere: the period is longer or shorter,

according to the velocity and direction of motion of the mark we take for reference in our observations ; this is all.

But if it is impossible to obtain the true period of rotation of Jupiter in the present condition of the planet, it is possible to approach it, and to come within narrow limits of the true period, by the observation of a great number of markings, having great permanency, and lasting unchanged for a long period, like the markings C, D, and E. It seems probable that this last, the great red spot, gives us, about as nearly as we ever can obtain it, the period of rotation of Jupiter ; although the period of this spot is far from being perfectly uniform, as it is certainly endowed with a motion of its own, which becomes very perceptible on some days, — a fact which is easily established from the changes of form of that spot described above. It is remarkable that the period of the red spot, greater at first, has decreased afterwards, and then increased at last so as to be very nearly equal to what it was at first. The mean period of this spot from Sept. 25 to Dec. 28, 1878, equals  $9^h 55^m 43.61^s$  ; from Aug. 9 to Nov. 9, 1880, it equals  $9^h 55^m 30.81^s$ , and from Nov. 9, 1880, to Feb. 13, 1881, it equals  $9^h 55^m 43.96^s$ . The mean intermediate period was then very nearly  $13^s$  shorter than were the first and last.

It is remarkable that of all the markings observed the red spot gives the greatest period of rotation to Jupiter ; next come the marks D and C, which also, like the red spot, had a long duration, and were on the south side and very nearly in the same latitude as this spot. These observations do not support the assumption, however, that the proper motion of the spots follows any law in regard to latitude, as is supposed to be the case with sun-spots ; for the spots G, which occupied about the same latitude in the north as the red spot occupied in the south, had a period over  $8^m$  shorter than has this last. The markings A, F, H, and I, although very nearly on the same parallel of south latitude, had different periods, the extreme of which differed by nearly  $6^m$ . The oval spot K, although in higher southern latitudes than the red spot, yet had a shorter period of rotation, and we have shown that the angular mark A, of 1876, observed on the southern border of the equatorial belt, had a period of  $2^h$  only, while all the markings of that hemisphere extending up to the pole had very nearly the same rapid proper motion. From the behavior of F, G, and H, it would seem that, all being equal, the period of rotation is shorter when the spot is new than when it has lasted for some time.

I have shown that the surface of Jupiter, like that of the Sun, has years of calm and years of great disturbance. In the year 1876, the

equatorial belt varied so much that on some days it appeared fully three times as broad as it did on others, extending to unusually high latitudes north and south, which at times reached  $40^{\circ}$  and  $45^{\circ}$  on either side of the equator. On several occasions, this broad, rosy equatorial belt did not appear symmetrically distributed on the sides of the equator, but was more or less one-sided, the southern being usually the side where it was most extended. In 1877, the disturbances on Jupiter were few and on a small scale, and after the middle of June the surface was remarkably quiet, the few changes noticed occurring principally within the equatorial belt. This state of quietness has continued till now, with the exceptions of the appearance of the red spot in 1878, which occurred without any great commotion or changes of the surface, and the bursting out of the row of round black spots in October, 1880, which subsequently developed into the broad rosy belt now seen in the northern hemisphere of the planet.

In regard to the question put forward by Mr. Marth, in the "English Mechanic," whether anything is known of the red spot in 1876-77, and whether it was then seen and observed, I can only give the following answer. In the year 1876 I began observing Jupiter on May 16, and observed it on every clear night as late as Oct. 19, and made during that interval 125 drawings of the planet. Nothing resembling the red spot in the slightest degree was seen during these observations. In 1877 the observations were begun on April 11, and continued on every clear night as late as Dec. 9, 142 drawings being made of its configuration, and no traces of the red spot were seen. In 1878, only a few observations were made before September; two drawings were made in February, two in March, one in May, one in June, and fifteen in September, previously to my seeing the red spot on the 25th of that month. My observations, therefore, do not give any information about this interesting object before Sept. 25, 1878. The negative evidence given by my observations amounts almost to certainty that the red spot did not exist before the year 1878.

CAMBRIDGE, March 5, 1881.

## XVII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF  
HARVARD UNIVERSITY.A PAPER ON THE PROPAGATION OF MAGNETIC  
WAVES IN SOFT IRON.

BY HAROLD WHITING.

Presented by Prof. Trowbridge, Feb 14, 1881.

WHEN a rapidly alternating current is made to pass through a coil of insulated wire wound about one end of a bar of soft iron, the latter becomes the seat of a series of magnetic waves, whose velocity and manner of propagation have, I think, not been determined.

The object of the present paper is to show that these waves differ in form, phase, and magnitude from the values assigned to them by any possible theory of instantaneous propagation; and that this rate of propagation, as determined by actual observation, is not generally very great, being measured in ordinary experiments by only a few feet, or at most a few hundred feet per second: but that no fixed velocity of propagation can be said to exist; since it depends largely upon the period of the wave, the material, dimensions, and accidental conditions of the bar, the distance from the magnetizing coil, and even, in extreme cases, upon the strength and distribution of the magnetic field.

In developing the complex laws which determine the velocity of propagation under so many variable conditions, I shall try also to show that the close analogy between magnetism, electricity, and heat, may be traced throughout the phenomena of magnetism in motion.

As early as the spring of 1876 I had completed, under the direction of Professor Trowbridge, a series of measurements supplementary to those of Mr. Rowland, showing the distribution of magnetism over a soft iron bar applied at one end to the pole of a permanent magnet. The subject next assigned to me was naturally the rate of this distribution, and of the propagation of magnetism in general.

A long half-inch bar was magnetized at one end by a (primary) coil connected with a battery. A small sliding secondary, of about 15 turns, was clamped at a short distance along the bar, and somewhat further off was placed a larger one, of about 150 turns.

The two coils were connected (in series) with a galvanometer so as to give opposed induction effects, and their relative distance was varied so that these effects should neutralize each other as nearly as possible.

It was found, as expected, that when the latter adjustment was made as accurately as possible, the spot of light thrown by the mirror of the galvanometer still made invariably a sudden motion, as if under the influence of the nearer of the two coils, followed by a sudden stop, due supposably to the somewhat tardier action of the more distant.

The interval of time between the two effects was estimated by various methods sufficiently obvious; the most successful being the actual determination of how rapidly the circuit must be closed and broken in order to reproduce, with a single secondary, the same effects as before. The various distances between the two secondaries, divided by the corresponding intervals of time, gave, of course, certain values of the velocity of propagation. These all lay within a few feet of 30 per second, for distances of not over one foot, beginning at 2 inches from the primary. How nearly these earlier estimates agree with the results of later investigation may be found below.

The method of measurement, however, is open to serious criticism, since the first sudden motion of the spot of light might be due to the small counter-current which ordinarily precedes the arrival of the normal current, and the magnitude of the counter-current would doubtless be greater in the larger of the two coils; so that the first sudden motion might really be due to the action of the more distant, rather than to that of the nearer coil. The experiments were, therefore, discontinued.

It was not until the autumn of 1880 that the experiments were again resumed, no new method less open to criticism having suggested itself in the mean time. I should, however, mention that certain experiments of Professor Trowbridge at Newport (which will doubtless be published in due time) had added both a confirmation of previous results and a renewed interest in the continuation of the investigation.

For the sake of continuity, the earlier experiments were repeated; then varied by the substitution of one secondary and two primaries

for two secondaries and one primary. Though the new method of procedure was open to the same objections as the old, the figures all agreed, within sufficiently narrow limits, both with themselves and with those before obtained. A telephone and musical contact-breaker were now substituted for the galvanometer and key. It was expected that the two sets of waves induced by a single primary in two secondaries, or by two primaries in a single secondary, could be made to interfere.

It was, of course, possible (upon any theory) so to place the two coils that each should neutralize very nearly the effect of the other, the telephone then being silent, and any considerable deviation from this position of the two coils must necessarily be accompanied by the production of a musical note; but, after long and unsuccessful search for *other* maxima and minima, the inevitable conclusion was reached that no true phenomenon of magnetic wave-interference could be found, and it was feared that all the previous results might have been delusive.

It was afterward discovered that, although the wave suffers a retardation, this retardation diminishes with the wave-length, so that it cannot produce complete interference under any condition whatsoever. We shall see, in fact, that the phenomena which have been described are perfectly consistent, the methods sound, and even that the rough measurements of these earlier experiments may be considered as close approximations to the truth.

The apparatus, principally employed in later and more precise determinations (see Diagram), consisted of a wooden shaft, one fourth inch in diameter, and about one foot long, carrying a pair of commutators (cut from a convenient size of brass tubing), — one of which was of the ordinary sort, the other different from it, in that its two arms were greatly prolonged, and at the same time twisted, corkscrew fashion, round the shaft one and one half turns each. The two lines of separation formed a pair of spirals of nearly constant pitch, so that by means of sliding contact-pieces this commutator might be made to act either simultaneously with its neighbor, or any fraction of a revolution sooner or later,\* and this without stopping the machine. One of the commutators was put in the primary, the other in the secondary, circuit. The primary, or magnetizing coil, was of No. 16 insulated wire, wound to a depth of half an inch over the first three inches of the

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\* This fraction of a revolution is called, later on, the inclination of, or angle between, the two commutators.

bar. The secondary was of No. 36 wire, wound upon a bobbin, with half an inch between its flanges, to a depth of about three eighths of an inch, and large enough to slide freely over the half-inch iron rod used in most of the experiments. A galvanometer, of somewhat greater resistance than the secondary coil, was also included in its circuit. The common shaft of the two commutators carried a fly-wheel and revolution-counter, and was set in motion by a pulley-wheel connected by a band with a powerful electric motor.

Though different in detail from the "Differential Interruptor" of Professor Blaserna (as described in Gordon's "Electricity and Magnetism," vol. i. p. 311 and ff.), this machine, though independently constructed, bears a most striking similarity to that of the Italian professor. The latter needs only the introduction of an iron core, common to the two secondaries, to fit it for the determinations which follow. The former is, however, adapted to the use of an alternating, instead of an intermittent, current, which gives for magnetic measurements a special advantage, and in determining not the slope of a given portion of the primary wave, but the value of the whole area enclosed by it, would consistently have been called by Professor Blaserna an "Integral Alternator." It being, however, the only *machine* employed in the phase-determinations which follow, I have alluded to it, when necessary, by its generic name.

When the shaft is set in rapid rotation, the bar is evidently magnetized; first positively, then negatively, &c. The period of time elapsing between two successive maxima of the same sign, in no matter what portion of the bar, evidently agrees with the length of time occupied by a single revolution of the commutator, and may be called the period of the magnetic wave. Each period repeats, of course, the same continuous series of changes as the one before it. The wave, accordingly, possesses a true *phase*; and the difference of phase of the magnetic wave at two different points in the bar may be defined as equal to the arc through which the shaft of the commutator must revolve, after the wave has reached a certain phase of its development in the one locality, in order that the tardier portion of the same wave in the other locality may attain the same, or rather a corresponding phase of *its* development. It is easy to find four corresponding points in the phase of any two waves; namely, the two maxima, positive and negative, and the two half-way points, or points of zero displacement. By means of one of the latter points the differences of phase were in all cases determined.

The current induced in the secondary coil would naturally flow one



way, while the magnetic wave is rising within it, and the other way, while falling; giving no effect, as a whole, upon the galvanometer. The second (adjustable) commutator, already alluded to, made it possible to "redress"\* these currents, so that they should *all* pass through the galvanometer in *either* direction. In fact, it was almost impossible so to adjust it that the current should *not* be turned, on the whole, a little one way or the other.

To avoid jarring, and direct action of the magnetism upon the galvanometer, whose deflections were to be noted, the machinery was removed as far as possible from the observer; while an assistant, according to direction, varied the angle between the two commutators, by means of the sliding-piece already alluded to, until the average deflection of the galvanometer was reduced to zero. Now the effect of the commutator in the secondary circuit is to add together all the pulses, positive and negative, which pass through it, in either of its two positions, to the galvanometer; and the symmetry of the wave, as regards positive and negative displacements, shows that the pulses are all alike; hence, each must be equal to zero when the total effect is zero. Since the magnitude of the pulse for a given interval of time is proportional to the rise or fall of the wave during that time, this rise or fall must also be equal to zero; that is, the initial and final displacements are identical: and hence (again from principles of symmetry) it is evident that, if there be no deflection of the galvanometer, every magnetic wave must have reached its mean height within the secondary coil at the instant of action of the (adjustable) commutator included in the circuit; so that comparison of these angles of adjustment for different velocities of the machinery, different distances between the two coils, and for different bars served to determine the various rates of propagation of the magnetic wave under these different conditions.

Earlier experiments gave discordant results, owing partly to imperfect contact within the commutator (which was afterward remedied as far as possible), but especially on account of the change of "magnetic conductivity" (if I may use the term) which the bar appeared to undergo after a few minutes of rapid and powerful magnetization and demagnetization. In one case, the conductivity appeared in consequence to increase two or three fold.

I should have been at some pains still further to investigate (or at least to confirm) this sensitiveness of soft iron to the influence of a

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\* In the sense of the French word, *redresser*.

strong alternating current, had I not been informed by Professor Trowbridge that experiments at Newport had already placed the matter beyond all doubt.

It had been supposed that only a powerful battery (ten or more Bunsen cells) would be able to give distinctly measurable results for the remote portions of the bar, whereas it now appeared that the conditions of success in these experiments depend upon the insufficiency of each current to produce a condition of magnetic saturation within the limited time of its action. The use of a single cell obviated all these difficulties, and was found to give sufficiently precise results for all portions of the bar.

In order to determine the several positions of the sliding-piece which corresponded to the simultaneous action of the two commutators, the shaft was set revolving very slowly, and the contact-piece was moved until the spot of light thrown by the galvanometer, though feeling every pulse, showed no constant deflection to right or left. A fixed pointer then covered, in each case, a certain division of a scale attached to the sliding-piece, the number of which being noted served as a zero for the calculation of angular measurements. The branches of the commutator making not quite one and one half turns, there were at most three points which satisfied this condition, one of which was taken as  $0^\circ$ , the next as  $180^\circ$ , and the third as  $360^\circ$ . Intermediate inclinations of the two commutators were measured by simple interpolation. Owing to the wearing away of the centres which supported the shaft, and their occasional readjustment, these three points had frequently to be redetermined.

The result of a long series of experiments\* upon a half-inch rod, some 53 inches long, was to show that the phase, in the portions of the bar not very remote from the primary, was *invariably later* than within the primary itself; and that this retardation increased up to a certain distance (not under 10 nor over 20 inches), to a maximum; and then diminished again, so that the furthest end of the bar did not differ in phase from the primary.

The phase of the primary was itself retarded more and more as the speed of the commutator increased, until for the highest velocities (100 or more reversals per second) it became fully equal to  $90^\circ$ , while the maximum retardation found anywhere in the bar never exceeded  $127^\circ$  or  $130^\circ$ ; and was, accordingly, never more than  $37^\circ$  or  $40^\circ$  later than the primary.

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\* See Table for Phase Retardation, appended.

The apparent velocity of propagation over the first seven inches of the bar ranged from 25 feet per second, for the low velocity of four reversals per second, up to 90 feet for about 23 reversals; after which it rose nearly in proportion to the number of reversals, until for 140 reversals it measured about 300 feet per second. At distances greater than 7 inches, the direct and instantaneous action of the primary and adjacent parts of the bar predominates more and more over the pulse propagated through the medium of the iron; so that the investigation of the rate of propagation in distant portions of the bar is not instructive. Indeed, since the most remote portions of the bar agree in phase with the primary, while intermediate portions lag behind it, we shall find the magnetic wave apparently flowing backward in the most distant portions. This, however paradoxical it may seem, is strictly in accordance with both theory and fact.

The following set of observations was dated Jan. 11:—

$c$  = the arbitrary position of the coil.

$ph$  = the position of the sliding-piece which gave zero deflection of the galvanometer.

$V$  = the number of ticks of a watch (beating 288 times to a minute) made while the shaft was performing 72 complete revolutions, and counted before and after each set of observations.

$V = 84 \quad - \quad - \quad - \quad 83.$		$V = 25 \quad - \quad - \quad - \quad 29.$	
$c = 0$	$ph = 14\frac{1}{2}$ mm.	$c = 0$	$ph = 18\frac{1}{2}$ mm.
1	$14\frac{1}{2}$ "	2	$19\frac{1}{2}$ "
2	$15\frac{1}{4}$ "	5	$20\frac{1}{2}$ "
3	$15\frac{1}{2}$ "	10	$21\frac{1}{2}$ "
4	$15\frac{3}{4}$ "	15	$22\frac{3}{4}$ "
5	$15\frac{1}{2}$ "	20	24 "
7	$16\frac{1}{2}$ "	25	24 "
10	$16\frac{1}{2}$ "	30	$23\frac{1}{2}$ "
15	$17\frac{1}{2}$ "	35	$22\frac{1}{2}$ "
20	$17\frac{3}{4}$ "	40	$21\frac{1}{2}$ "
30	$16\frac{1}{2}$ "	45	$20\frac{1}{2}$ "
45	...	48	$19\frac{1}{2}$ "
10	$16\frac{1}{2}$ "		
0	$14\frac{1}{2}$ "		

The first point of simultaneous action was  $10\frac{1}{2}$  mm., the second  $29\frac{1}{2}$  mm., and the third  $38\frac{1}{2}$  mm. The distances were reckoned in inches, beginning at a point 2 inches from the centre of the primary.

Hence we get the following tables, where  $v$  = the number of revolutions per second,  $t$  = the length of time occupied by the wave in reaching the distance,  $d$ , measured in inches from the centre of the primary:—

$v = 4.$		$v = 14 \dots 12.$	
$t = .028$	$d = 2$	$d = 2$	$t = .015$
3	.028	4	.017
4	.029	7	.020
5	.029	12	.021
6	.031	17	.024
7	.034	22	.027
9	.037	27	.028
12	.037	32	.027
17	.042	37	.025
22	.044	42	.023
32	.038	47	.022
47	...	50	.020
12	.037		
2	.024		

The following observations, taken with a break corresponding to the removal of the first 10 inches of the bar, bear also the same date:—

$V = 26.$		$v = 13.$	
$c = 10$	$ph = 15\frac{1}{2}$ mm.	$d = 12$	$t = .010$
15	19 "	17	.016
20	18 $\frac{1}{2}$ "	22	.016
30	19 $\frac{1}{2}$ "	32	.016
48	19 "	50	.016

showing that the interruption of a large portion of the pulse of propagation is accompanied by a much less retardation of the phase. There was reason to believe that only about half of this pulse was interrupted in this way. All attempts to measure the amount of the *direct* pulse have given widely different results; and the rough experiments, upon which the above opinion was founded, do not deserve special notice.

The phenomena are essentially the same for a short bar of about 20 inches in length; that is, of course, as far as they go. In the notation used above, the results are reduced as follows:—

$d = 2$	$v = 4.5$	$v = 14.5$
	$t = .018$	$t = .012$
3	.021	.013
4	.022	.015
5	.023	.016
6	.024	.016
7	.025	.018
9	.028	.018
12	.033	.020
17	.034	.021

A small rod of one fourth inch diameter was now substituted, and much smaller differences of phase were obtained, corresponding to the

same speed of the commutator. A steel bar, one half inch in diameter, gave nearly the same results as the one fourth inch rod of soft iron, but the highest velocities were not used with any of them. It was, however, determined for both that an increase of electromotive force causes a considerable increase in the retardation, but apparently affects the soft iron more in the nearer, and the steel in the further, portions.

Little reliance can be placed in determinations for distances above 20 inches; but it would seem probable, from the experiments below, that the anomalous behavior of the steel is due to "coercive force," which in the most distant parts gives way only under the influence of a powerful battery, while that of the soft iron is due to super-saturation, which can exist only in the nearer portions.

It appears, also, from the experiments, that the "magnetic conductivity" of the steel cannot be far from a fourth of that of the soft iron.\*

TABLE FOR HALF-INCH STEEL ROD.

 $V = 81 - - - 86.$ 

$c = 0$	(1 Cell.)	(10 Cells.)
	$ph = 12.7 \text{ mm.}$	$ph = 12.6 \text{ mm.}$
1	13.0 "	13.1 "
2	13.2 "	13.4 "
3	13.2 "	13.5 "
4	13.2 "	13.6 "
5	13.2 "	13.6 "
7	13.2 "	13.6 "
10	13.4 "	13.6 "
15	13.6 "	13.6 "
20	13.6 "	13.6 "
30	13.7 "	13.7 "

 $V = 20 - - - 22.$ 

$c = 0$	(10 Cells.)	(1 Cell.)
	$ph = 15.6 \text{ mm.}$	$ph = 16.0 \text{ mm.}$
1	16.2 "	16.6 "
2	16.7 "	16.9 "
3	16.9 "	17.4 "
4	17.1 "	17.5 "
5	17.6 "	17.8 "
7	18.0 "	18.2 "
10	18.4 "	18.7 "
15	19.0 "	18.5 "
20	19.5 "	17.7 "
25	21.0 "	...
30	24.7 "	14.5? "

\* See "Rowland's Tables of Permeability of Steel and Iron," American Journal of Science, 1873.

TABLE FOR QUARTER-INCH IRON ROD.

$$V = 24 \text{ --- } 27.$$

$c = 0$	(1 Cell.)	(4 Cells.)
	$ph = 13.0 \text{ mm.}$	$ph = 16.0 \text{ mm.}$
5	13.5 "	17.7 "
10	14.0 "	18.8 "
15	18.7 "	18.5 "
20	17.5? "	16.1 "
30	... "	16.7 "

The zero points were 10.5 mm., 29.5 mm., and 38.5 mm., nearly, as before.

No experiments have as yet been made upon nickel or cobalt, the stress of the whole investigation having been thrown upon soft iron. The results of a long series of experiments similar to those quoted above, with slight modifications introduced by the method described below, and corrected as far as possible by the ordinary processes of differencing, are embodied in the large Table for Phase Retardation at the end of this paper. A set of curves of constant retardation are also given.

Although these experiments were conducted with the greatest exactness possible with the rough apparatus employed, they were open to criticism in that they were separated by long intervals of time, and possibly subject to wide variations of condition. To confirm their general results, and in a manner to leave no doubt that the retardation of phase really depends upon the speed of the commutator (the other conditions being constant), so as to gradually disappear and reappear with the diminution and increase, respectively, of its velocity, an electric motor was employed, whose revolving wheel was heavy enough to keep itself and the commutator in motion for a long time after the electricity had been cut off. In coming thus gradually to rest, all velocities between maximum and zero must have been passed through, thus affording the best possible opportunity for a close comparison.

Meantime, each swing of the galvanometer was noted (its period being made sufficiently great), as well as the exact time of stopping of the machine, obtained by a sharp signal from an assistant. The mean between two successive points of turning gave the average deflection of the galvanometer for the interval of time between them; and knowing the length of time of each swing (a constant), the rate of stopping of the machine (nearly constant), and the exact time of

its coming to rest relatively to the last recorded swing, it was easy to calculate the number of revolutions per second corresponding to a given deflection.

Taking different distances along the bar, as well as different inclinations of the two commutators, over a thousand determinations were made in the course of a few days. The result was in general a confirmation of the previous and more exact experiments.

In many cases an actual reversal of the current took place during the period of stopping of the machine; but of course when the inclination of the commutators was such that a reversal would indicate a retardation of more than the maximum found before, no such reversal took place.

These experiments serve, moreover, nicely to illustrate the fact upon which all thorough understanding of the above phenomena is based, namely, that magnetism requires a fixed time to reach a fixed value, and a greater time, proportionally, for greater distances from the magnetizing coil; so that, with even the moderate velocities employed (20 to 30 reversals per second), it has not time enough to reach its maximum even within the primary itself between two successive reversals; and for still shorter intervals of time reaches a proportionally less value.

This is proved by the fact that, when the commutators are adjusted to best advantage, the deflection of the galvanometer is independent of the speed of the commutator within certain limits, as 5 to 12 revolutions, or 10 to 24 reversals per second, after which it falls off a little; gradually diminishing more and more nearly in proportion to the increase in velocity, until, at 140 reversals, it is reduced to a quarter or a thirtieth of its maximum value, the diminution being most marked for distances moderately remote. For, if each wave had time to reach its maximum, the deflection, instead of diminishing, would increase in direct proportion to this velocity, as is indeed the case when the velocity is only a few turns per second. The actual results are contained in the Table of Galvanometer Deflections, which is appended.

It is evident that, by dividing the deflections contained in this table by the corresponding number of revolutions of the commutator, we obtain a series of numbers proportional to the actual height of each wave at the end of the short intervals of time during which the current acted. In the table below, the first column shows the duration of each current in terms of an arbitrary unit; the second column shows the corresponding height of the wave at a distance of two inches from the primary, expressed in percentages of that height



which it would finally have attained had the current not been cut off. The third column expresses similarly the percentage magnetization after different intervals of time at a distance of 14 inches along the bar. The fourth column is taken from a table in Jenkin's "Electricity and Magnetism," page 330, and expresses the percentage electrification at the end of a cable, also in terms of an arbitrary unit. The value of this unit for the French Atlantic cable is given as 0.196 seconds. The magnetic value of this unit for a distance of two inches over our bar is 0.010 seconds, and for fourteen inches 0.013 seconds nearly, or about one fifteenth of the electric value for the whole Atlantic cable. From this an idea can be formed of the greatness of magnetic, as compared with electric, resistance.

TABLE OF PERCENTAGE MAGNETIZATION AS DEPENDENT  
UPON THE TIME.

$t : a =$	$d = 2$	$d = 14$	For Electricity.
1.1	3.0	0.045	0.04
2.3	13.0	0.63	4.6
3.8	...	7.2	22.0
4.1	...	8.0	26.0
4.5	...	17.0	32.0
5.0	42.0	19.0	39.0
5.6	46.0	32.0	46.0
6.5	64.0	38.0	55.0
7.5	68.0	59.0	64.0
8.5	72.0	67.0	74.0
13.0	88.0	87.0	89.0

Of course it is not possible to expect close agreement of our results with those obtained for electricity. It is true that every law of magnetic induction may be said to correspond to one in electric conduction; and similarly we may expect that the laws of the establishment of magnetic induction (propagation of magnetism) will correspond to those of the establishment of the electric current. But we must remember that a bar magnetized at one end really corresponds not to a perfectly, but to an imperfectly, insulated cable, the laws for which I have not been able to find anywhere developed. The apparent agreement of the third and fourth columns of our table at the extremes, and to so large an extent elsewhere, is certainly remarkable whether accidental or not.

The table shows that the form of the magnetic wave at a moderate distance from the primary is similar to that of the electric wave at the end of a long cable, but that as we approach the primary the roundness disappears, so that a rapid series of waves would present more

or less sharpened crests and troughs. In no case, however (except for the lowest possible velocities), would the wave approximate to the rectangular form assigned to it by the theory of instantaneous action; nor, since its form differs at different distances, can it conform to any theory of instantaneous propagation.

The table also enables us to estimate the length of time that elapses before the wave can reach its mean height within the secondary when placed as near as possible (say two inches) to the centre of the primary. The time is about .058 seconds. This large retardation accounts for certain discrepancies found in earlier determinations of the zero points by the use of insufficiently low velocities.

The table shows, moreover, the actual velocity of propagation. We find, *e.g.*, that the time occupied by a point at fourteen inches in reaching fifty per cent of its maximum magnetization is about .035 seconds greater than for a point at two inches, giving a velocity of about twenty-eight and a half feet per second, which agrees as closely as could be expected with early results. For other percentages of magnetization we should of course obtain different results; but this particular result is of special significance in that it represents, in a measure, the rate of propagation of the body of the pulse. It may conveniently be termed the *principal velocity* of the magnetic wave.

The last method of measurement is likewise adapted to the use of a dynamometer (the phase-adjustment being a hinderance rather than a help); and is really an independent way of determining the velocity of propagation.

There is still another method of arriving at this velocity. If in the Table for Phase-Retardation, we subtract the phase for two inches from that for fourteen, and divide by the whole number of degrees described by the commutator in a second, we shall have the length of time occupied by the phase of mean height of the wave in travelling over the same twelve inches of the bar. The lowest possible velocity of revolution must be chosen in order to approximate to our former conditions.

Taking two revolutions per second, we find a difference of  $24^\circ$ , corresponding to one thirtieth of a second; whence the velocity is thirty feet per second, nearly as before.

The following is a series of velocities computed in the same way, each over six inches of the bar, beginning at 0, 2, 4, &c., inches:—

<i>d.</i>	<i>V<sub>y</sub>.</i>	<i>d.</i>	<i>V<sub>y</sub>.</i>	<i>d.</i>	<i>V<sub>y</sub>.</i>
0	33	16	120	32	-45
2	26	18	180	34	-40
4	28	20	∞	36	-45
6	30	22	-180	38	-40
8	36	24	-120	40	-40
10	45	26	-90	42	-40
12	72	28	-60	44	-60
14	90	30	-51	46	-90
				..	∞

The minimum positive velocity has, of course, the greatest significance, being most free from the effects of direct action; and we may finally conclude that the "principal velocity" of propagation of the magnetic wave over a half-inch rod, unaffected by foreign influence, is in the neighborhood of twenty-five feet per second. The "principal velocity" of the electric pulse over the French Atlantic cable is about 13,700,000 feet per second.

Besides the experiments already alluded to, there was a preliminary series made with a Siemens armature machine, — the armature being converted into a powerful electro-magnet, and caused to revolve by means of a band and pulley-wheel. A series of magnetic waves was induced in the fixed horseshoe between whose poles the armature revolved; and, on screwing an iron rod firmly into one of its extremities, the waves spread more or less over the bar. A small induction coil was placed around the bar at a distance of sixteen inches, and connected with the galvanometer through a commutator which acted at the moment when the armature reached the position of greatest attraction. It is evident that, when the machine was set revolving very slowly, the impulses were all added together. It was found, however, as expected, that, as the velocity increased, the deflection of the galvanometer diminished, and was finally completely reversed, showing that a retardation of more than  $90^\circ$  of phase must have taken place. The least velocity which could cause a reversal was usually about fifteen revolutions per second, — although the number varied greatly at different times. It is interesting to observe that this velocity and distance correspond to a retardation of phase, in our table, of  $108^\circ$ .

It was thought that by this method the uncertainty of the time of magnetization of a primary coil would be got rid of, since the exact time of each impulse could be known; but the imperfection of the apparatus and discordance of the results caused this method to be abandoned.

The phenomena of the propagation of the magnetic wave in a bar

of soft iron are complicated by the fact that in addition to the pulse which reaches a given point at a given time, necessarily later than the time of its starting, there is another pulse, due to the direct action of the primary and adjacent parts; a pulse which at great distances becomes, as before stated, indefinitely large in comparison with the former. This will be evident on considering the nature of the two curves which represent the action of each pulse. The direct pulse decreases, of course, as the cube of the distance increases; while the logarithm of the pulse propagated through the bar, as determined by actual experiment, becomes regularly less in proportion to the distance. For a distance of fifty inches on our half-inch bar, whose coefficient of retained magnetism was 0.77 per linear inch, we have the direct pulse, by calculation, some three and three-fourths times greater than the indirect; so that, no matter what be its difference of phase, the effect cannot greatly exceed a retardation of  $15^\circ$ , and the point of maximum retardation, which was more than  $40^\circ$ , must lie somewhere on the bar. This was, as we have seen, the fact. It is easy to show, moreover, that this point cannot be nearer the primary than the point where the ratio of the indirect pulse to the direct (which it greatly exceeds) is at its maximum; and the latter is found by calculation to be at about 11.6 inches. The actual position of the point of maximum retardation of the phase lay always between these two limits.

As regards the phase of the primary itself, it is easily shown that since the increase of its magnetism determines an electromotive force opposed to that of the battery, which it cannot exceed, its rate of magnetization is determined for short intervals of time by that electromotive force; and that, in consequence, the magnetism keeps pace with the time.

In the differential equation

$$dm = \frac{\log^{-1}}{k} \left( \log E - \frac{Rt}{k^2} \right) dt;$$

put  $t = 0$ , and we have

$$m = \int \frac{E}{k} dt = \frac{E}{k} t,$$

the constant of integration being zero; this value of  $m$  being a special solution of the general integral,

$$m = \int_0^t \frac{\log^{-1}}{k} \left( \log E - \frac{Rt}{k^2} \right) dt = -\frac{Ek}{R} \left( \frac{1}{\log^{-1} \frac{Rt}{k^2}} \right) + \frac{Ek}{R},$$

where  $m$  = the magnetization,  $k$  = a constant depending upon the length, shape, etc., of the coil,  $R$  = the resistance of the primary circuit, and  $t$  = the duration of the current.

The phase of mean height will therefore be just half-way between that of maximum and minimum, or  $90^\circ$  later than it would have been were the rise of the magnetic wave instantaneous.

The phase is still more retarded in moderately distant portions of the bar, because the magnetization there depends, not merely upon the direct pulse, but also upon displacements already existing in the bar; but since these displacements agree in phase with the primary, and totally disappear with the return of the wave to its mean height, and since these displacements cannot exert a much greater influence than the primary itself (which causes them), the greatest possible retardation of phase due to these secondary effects cannot greatly exceed  $45^\circ$  or  $50^\circ$ , and may not reach that limit. We need not therefore be surprised that the total retardation is limited to  $90^\circ$  plus the above amount, or, in practice, to  $130^\circ$ .

I have left out all discussion of the oscillations of the induced current, since these will not, as a whole, interfere with the results. They are discussed in Gordon's "Electricity and Magnetism," vol. i. page 311 et seq.

I have already alluded to the experiments of Professor Blaserna upon a subject so closely allied to my own. The determination of the interval of time between the establishment of the primary current and the establishment of the induced current gives rise to a series of values of the rate of propagation of the pulse through air and other non-conductors, just as my own experiments have endeavored to do through iron. The results of the latter would indicate that the assumption apparently made by Professor Blaserna that the rate of propagation through air, etc., is constant, is at least open to criticism.

The obvious application of the results of the above investigation to the Gramme ring, the construction of electro-magnetic engines, and the whole subject of magneto-acoustics, I am obliged, for the present, to leave untouched; together with the exact mathematical solution of the problem of phase-retardation.

We have seen that magnetism, like electricity, can be said to have no proper velocity; that when one end of a conductor is magnetized or electrified, the other begins instantaneously to feel an influence, however slight; that the electric or magnetic pulse is not measurable for a short time, then rises very rapidly with the increase of time, then less and less rapidly, and finally becomes constant. Not only

qualitatively are the two sets of phenomena alike, but also, to a large extent, quantitatively; and there are reasons more than sufficient to account for their differences. We are led, therefore, to conclude that the laws of magnetic propagation are in all probability the same as, or very similar to, those of the establishment of the electric current; and consequently to the corresponding laws of heat.

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### SUMMARY.

I. The magnetic waves induced in a bar of soft iron by an alternating current differ in form, phase, and magnitude from the values assigned to them by any theory of instantaneous propagation.

II. They differ in form, inasmuch as the rise and fall of the magnetic wave is in no case abrupt; but it presents, even for a moderate number of reversals to the second, a perfectly rounded crest and trough, especially at considerable distances from the primary.

III. The magnitude of the waves is constant up to five or six reversals per second, after which it is much lessened; from twenty to thirty reversals, it diminishes nearly with the number of reversals (the deflection of the galvanometer remaining constant); from fifty to one hundred and forty it falls off more and more rapidly, especially for moderate distances along the bar, being there reduced so as to give about one thirtieth of its former maximum deflection.

IV. The phase within the primary is retarded more and more as the rapidity of alternation of the current increases,—to a maximum of  $90^\circ$ , and for a distance not too remote is invariably later than it is within the primary.

V. The apparent retardation of the phase depends upon the period (length) of the wave; the arbitrary distance from the primary; the material, dimensions, and special condition of the bar; and even, in extreme cases, upon the strength and distribution of the magnetic field.

VI. The retardation increases for a certain distance (about thirty diameters) to a maximum of from  $127^\circ$  to  $130^\circ$ ; or from  $37^\circ$  to  $40^\circ$  later than that of the primary; falling, again, gradually, at great distances, to  $90^\circ$ , that is to the original value within the primary itself.

VII. The apparent velocity of propagation, accordingly, increases

from a moderate value, in parts of the bar not too remote, to infinity, somewhere in its central portion, and then descends with change of sign, for a still further advance in distance, to a minimum, and finally becomes infinite again; so that, the most distant portions of the wave reaching their maximum height simultaneously with the nearest, the wave appears to flow backward over the most distant part of the bar.

VIII. The apparent velocity of propagation over the first fourteen diameters is from twenty-five feet per second, corresponding to four reversals per second, up to ninety feet, for twenty-three reversals, after which it rises nearly in proportion to the number of reversals, until, for one hundred and forty reversals, it measured about three hundred feet per second.

IX. The magnetic conductivity of the bar increased (in one case from two to three fold) under the continued influence of the alternating current sent by a high electromotive force, whose use in these determinations must generally be avoided.

X. The retardation of phase is less for small rods than for large ones, but in most respects the effects are similar for distances proportional to the relative diameters of the bars.

XI. The retardation is less for steel than for iron. With steel, a high electromotive force may be advantageously employed to overcome the tendency of the magnetic displacements to become permanent.

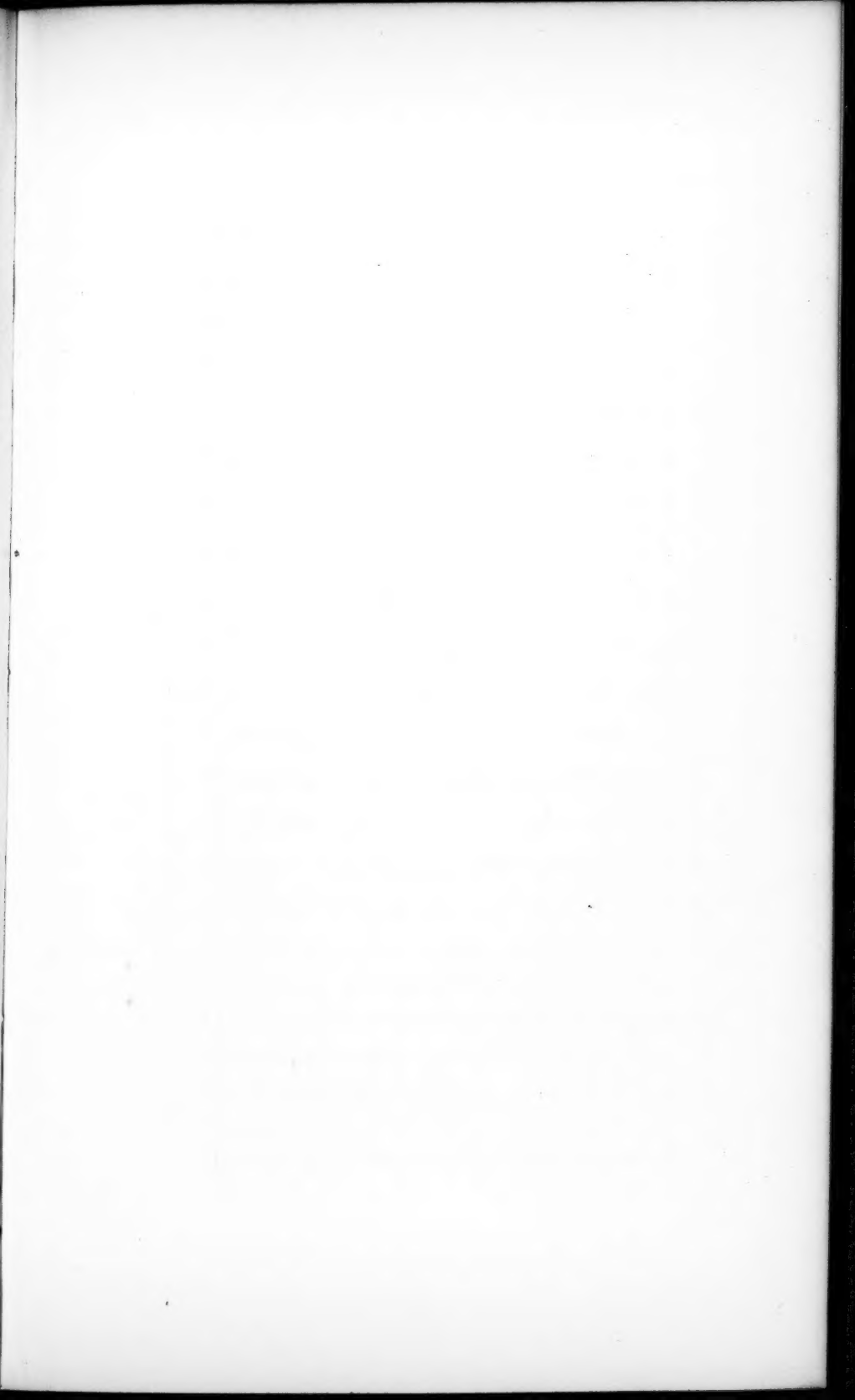
XII. The phase of the magnetic wave may be treated as the resultant of that of two sets of waves, one due to the direct (and instantaneous) action of the primary itself, and proportional, accordingly, to the time and to the inverse cube of the distance; the other depending upon the secondary effect of magnetism already induced in the bar, and hence proportional more or less to the square and higher powers of the time, and to the distance as the exponent of a constant factor, less than unity. In the same way that each law of magnetic induction has a parallel in the conduction of electricity, it is probable that the law of change in the one is similar to the law of change in the other.

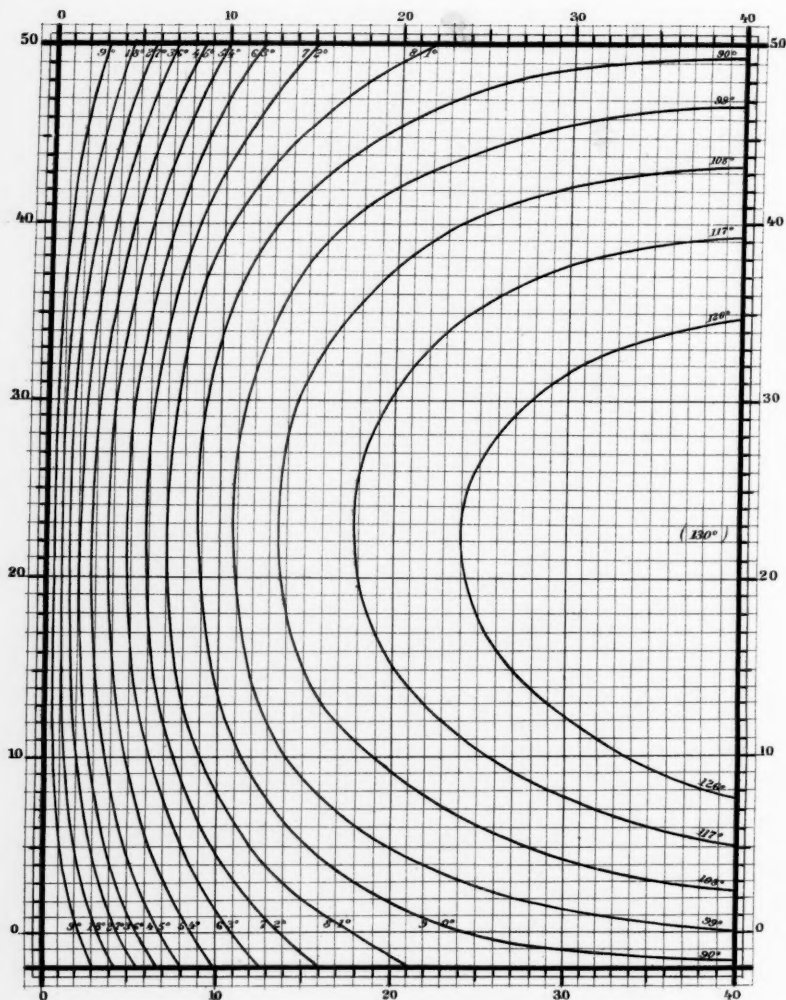


TABLE FOR PHASE-RETARDATION.\* (For mean height.)

$v =$	52	50	48	46	44	42	40	38	36	34	32	30	28	26	24	22	20	18	16	14	12	10	8	6	4	2	0	$v =$
$d =$	52	50	48	46	44	42	40	38	36	34	32	30	28	26	24	22	20	18	16	14	12	10	8	6	4	2	0	52
	0	8	20	34	47	60	72	83	93	100	105	108	110	111	111	111	111	111	111	111	111	111	111	111	111	111	87	52
	0	9	23	38	53	65	77	84	88	92	96	99	100	100	100	100	100	100	100	100	100	100	100	100	100	100	95	50
	0	11	27	43	58	70	82	89	93	97	100	102	103	103	103	103	103	103	103	103	103	103	103	103	103	103	107	48
	0	14	32	48	63	75	87	93	97	102	104	106	107	107	107	107	107	107	107	107	107	107	107	107	107	107	111	46
	0	18	36	54	68	80	91	96	98	102	104	106	108	109	109	109	109	109	109	109	109	109	109	109	109	109	115	42
	0	20	40	58	72	83	91	96	101	104	107	110	113	114	114	114	114	114	114	114	114	114	114	114	114	114	115	40
	0	23	43	61	76	86	94	99	104	107	110	113	115	117	117	117	117	117	117	117	117	117	117	117	117	117	119	38
	0	26	46	64	79	89	96	102	106	110	113	115	118	120	121	122	122	122	122	122	122	122	122	122	122	122	124	36
	0	29	50	68	82	91	99	105	109	112	115	118	120	122	124	125	125	125	125	125	125	125	125	125	125	125	126	34
	0	31	52	70	83	93	100	106	110	114	118	121	122	124	125	126	126	126	126	126	126	126	126	126	126	126	127	32
	0	33	54	71	84	94	101	107	112	115	119	122	124	125	126	126	126	126	126	126	126	126	126	126	126	126	127	30
	0	35	56	73	85	95	102	108	113	117	119	122	124	125	126	126	126	126	126	126	126	126	126	126	126	126	127	28
	0	38	58	75	87	97	104	109	113	118	120	123	125	126	126	126	126	126	126	126	126	126	126	126	126	126	127	26
	0	40	60	77	89	99	106	111	115	119	121	123	125	126	126	126	126	126	126	126	126	126	126	126	126	126	127	24
	0	42	62	79	91	100	107	112	116	120	122	124	125	126	126	126	126	126	126	126	126	126	126	126	126	126	127	22
	0	44	64	81	93	102	109	114	118	122	124	125	126	126	126	126	126	126	126	126	126	126	126	126	126	126	127	20
	0	46	66	83	95	104	111	116	120	123	125	126	126	126	126	126	126	126	126	126	126	126	126	126	126	126	127	18
	0	48	68	85	97	106	113	118	122	124	125	126	126	126	126	126	126	126	126	126	126	126	126	126	126	126	127	16
	0	50	70	87	99	108	115	120	124	126	127	127	127	127	127	127	127	127	127	127	127	127	127	127	127	127	127	14
	0	52	72	89	101	110	117	122	126	128	129	129	129	129	129	129	129	129	129	129	129	129	129	129	129	129	129	12
	0	54	74	91	103	112	119	124	128	130	130	130	130	130	130	130	130	130	130	130	130	130	130	130	130	130	12	10
	0	56	76	93	105	114	121	126	130	132	132	132	132	132	132	132	132	132	132	132	132	132	132	132	132	132	12	8
	0	58	78	95	107	116	123	128	132	134	134	134	134	134	134	134	134	134	134	134	134	134	134	134	134	134	12	6
	0	60	80	97	109	118	125	130	134	136	136	136	136	136	136	136	136	136	136	136	136	136	136	136	136	136	12	4
	0	62	82	99	111	120	127	132	136	138	138	138	138	138	138	138	138	138	138	138	138	138	138	138	138	138	12	2
	0	64	84	101	113	122	129	134	138	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140	12	0
	0	66	86	103	115	124	131	136	140	142	142	142	142	142	142	142	142	142	142	142	142	142	142	142	142	142	12	0
	0	68	88	105	117	126	133	138	142	144	144	144	144	144	144	144	144	144	144	144	144	144	144	144	144	144	12	0
	0	70	90	107	119	128	135	140	144	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	12	0
	0	72	92	109	121	130	137	142	146	148	148	148	148	148	148	148	148	148	148	148	148	148	148	148	148	148	12	0
	0	74	94	111	123	132	139	144	148	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150	12	0
	0	76	96	113	125	134	141	146	150	152	152	152	152	152	152	152	152	152	152	152	152	152	152	152	152	152	12	0
	0	78	98	115	127	136	143	148	152	154	154	154	154	154	154	154	154	154	154	154	154	154	154	154	154	154	12	0
	0	80	100	117	129	138	145	150	154	156	156	156	156	156	156	156	156	156	156	156	156	156	156	156	156	156	12	0
	0	82	102	119	131	140	147	152	156	158	158	158	158	158	158	158	158	158	158	158	158	158	158	158	158	158	12	0
	0	84	104	121	133	142	149	154	158	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	12	0
	0	86	106	123	135	144	151	156	160	162	162	162	162	162	162	162	162	162	162	162	162	162	162	162	162	162	12	0
	0	88	108	125	137	146	153	158	162	164	164	164	164	164	164	164	164	164	164	164	164	164	164	164	164	164	12	0
	0	90	110	127	139	148	155	160	164	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	12	0
	0	92	112	129	141	150	157	162	166	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	12	0
	0	94	114	131	143	152	159	164	168	170	170	170	170	170	170	170	170	170	170	170	170	170	170	170	170	170	12	0
	0	96	116	133	145	154	161	166	170	172	172	172	172	172	172	172	172	172	172	172	172	172	172	172	172	172	12	0
	0	98	118	135	147	156	163	168	172	174	174	174	174	174	174	174	174	174	174	174	174	174	174	174	174	174	12	0
	0	100	120	137	149	158	165	170	174	176	176	176	176	176	176	176	176	176	176	176	176	176	176	176	176	176	12	0
	0	102	122	139	151	160	167	172	176	178	178	178	178	178	178	178	178	178	178	178	178	178	178	178	178	178	12	0
	0	104	124	141	153	162	169	174	178	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180	12	0
	0	106	126	143	155	164	171	176	180	182	182	182	182	182	182	182	182	182	182	182	182	182	182	182	182	182	12	0
	0	108	128	145	157	166	173	178	182	184	184	184	184	184	184	184	184	184	184	184	184	184	184	184	184	184	12	0
	0	110	130	147	159	168	175	180	184	186	186	186	186	186	186	186	186	186	186	186	186	186	186	186	186	186	12	0
	0	112	132	149	161	170	177	182	186	188	188	188	188	188	188	188	188	188	188	188	188	188	188	188	188	188	12	0
	0	114	134	151	163	172	179	184	188	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	12	0
	0	116	136	153	165	174	181	186	190	192	192	192	192	192	192	192	192	192	192	192	192	192	192	192	192	192	12	0
	0	118	138	155	167	176	183	188	192	194	194	194	194	194	194	194	194	194	194	194	194	194	194	194	194	194	12	0
	0	120	140	157	169	178	185																					

\* See note under next table, also page 327 et seq.

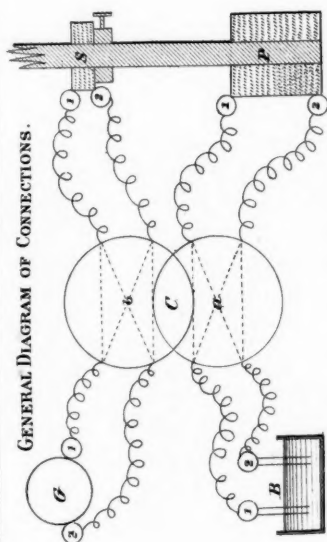




**CURVES OF CONSTANT PHASE RETARDATION.**

*See Table for Phase Retardation.*

GENERAL DIAGRAM OF CONNECTIONS.



*B* = the battery.  
*P* = the primary.  
*S* = the secondary.  
*G* = the galvanometer.  
*C* = the commutators.  
 (a) in primary circuit.  
 (b) " secondary "

*r* = the revolution counter.  
*f* = the fly-wheel.  
*w* = the contact-wheel.  
*t* = the contact pieces.  
*s* = the sliding piece.

Subscript numerals  
 denote connections.

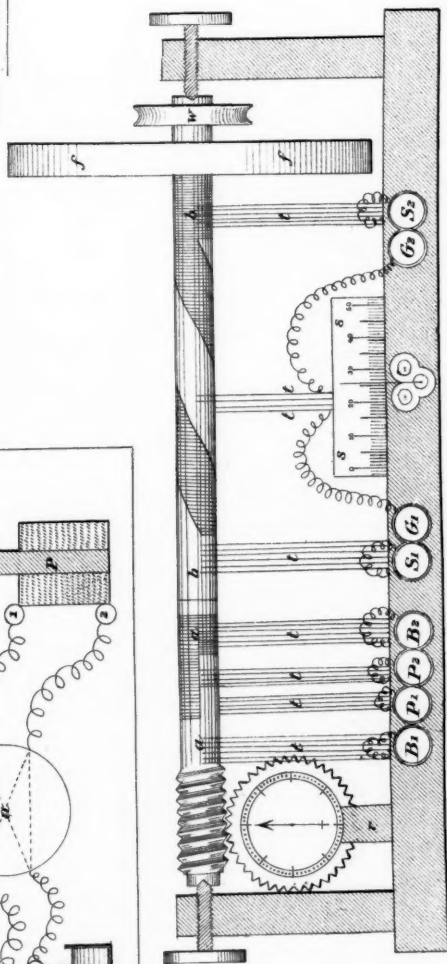


DIAGRAM OF THE DOUBLE COMMUTATOR SHOWING ITS INTERNAL CONNECTIONS.

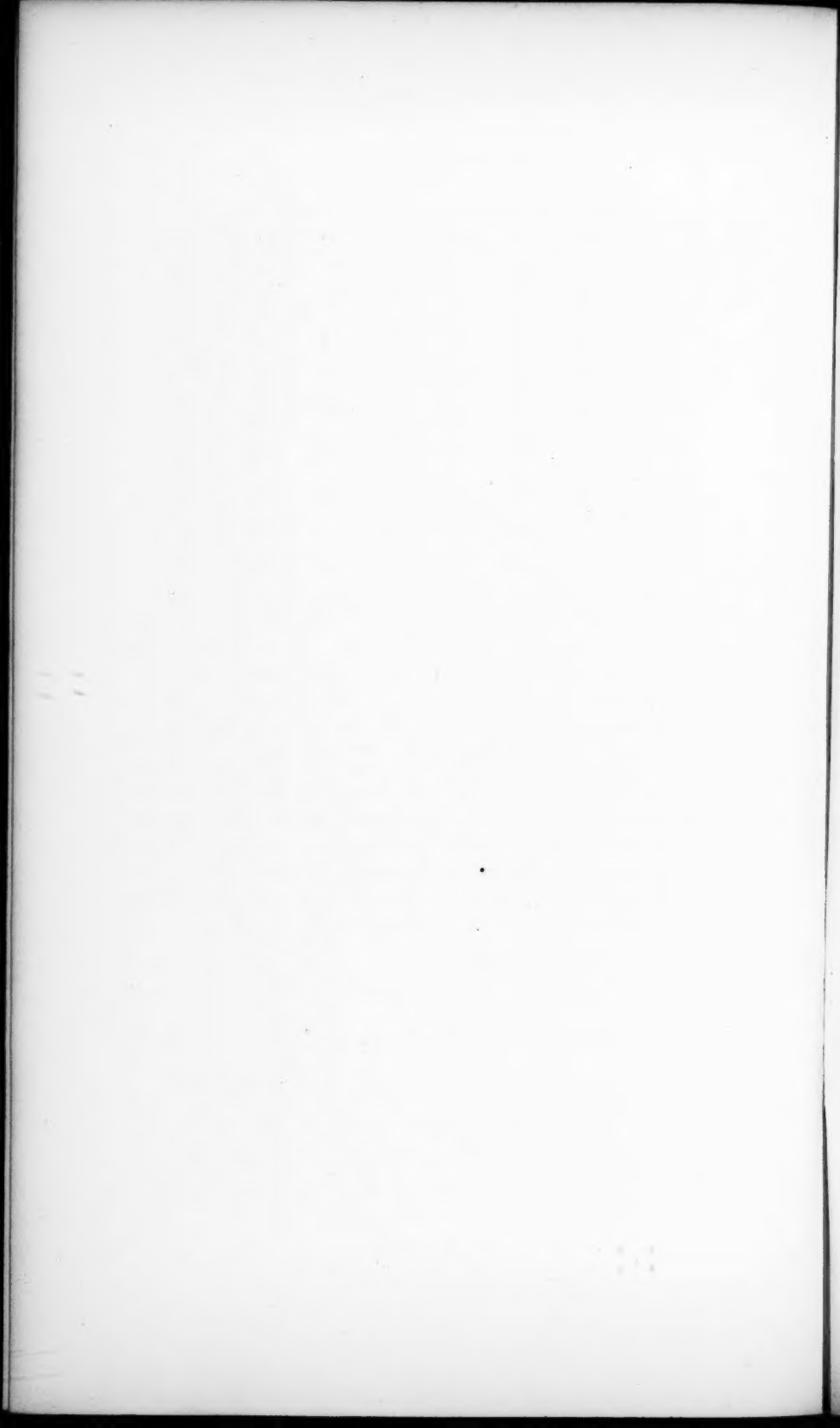


TABLE OF GALVANOMETER DEFLECTIONS

	<i>d</i> = 2	5	9	14	22	32	47
<i>v</i> = 1.6	5	5	4	1	0.3	.020	.000
3.3	12	11	8	2	0.6	.038	.005
5.0	20	16	10	3	0.9	.057	.008
6.6	27	21	11	4	0.9	.072	.012
8.7	33	28	11	4	0.9	.090	.013
10.0	32	28	11	4	0.9	.081	.014
11.6	38	28	12	3	0.8	.081	.015
13.3	41	26	13	3	0.8	.081	.015
15.0	43	25	11	2	0.7	.081	.015
16.6	42	24	10	2	0.7	.081	.014
18.3	39	23	8	1	0.6	.079	.014
20.0	36	21	7	1	0.5	.079	.014
( <i>v</i> = 0)	1.37	0.69	0.24	0.06	0.01	.001	...
	<i>d</i> = 2	5	9	14	22	32	47

The phase retardation is measured in degrees, one whole phase (or period between two successive maxima or minima) being taken as  $360^\circ$ . The galvanometer deflections (see page 332 et seq.) are reduced to a common unit through the known ratio of various shunts, the greatest divisor being two hundred. The deflections due to a single closing of the circuit, always in the same direction, are placed in line with " $v = 0$ ." The divisions of the scale were about 5 mm. apart.  $d$  and  $v$  represent in both tables the distance in inches between the coils, and the velocity in revolutions per second. The galvanometer deflections are, of course, only approximate; but for small distances and low velocities, the probable error of the phase-retardation will not greatly exceed  $5^\circ$ . The curves of constant phase-retardation, at intervals of  $9^\circ$ , are represented, graphically, below;  $d$  and  $v$  being understood as vertical and horizontal coördinates.

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INVESTIGATIONS ON LIGHT AND HEAT, made and published wholly or in part with appropriation from the RUMFORD FUND.

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## XVIII.

## THE BOLOMETER AND RADIANT ENERGY.

BY PROF. S. P. LANGLEY.

Presented Jan. 12, 1881.

OUR knowledge of the distribution of heat in the solar spectrum really begins with this century and the elder Herschel, and, since his time, great numbers of determinations have been made, all with scarcely an exception, by means of the prism, the early ones through the thermometer, the later ones by the thermopile and galvanometer. It was very soon seen that the prism exercised a selective absorption, and that the form of the heat-curve varied with the material of the refracting substance, but a far more important and more subtle error was left almost unnoticed. The elder Draper, I believe, long since pointed out that the prism, contracting as it does the red end, and still more the ultra-red, gives false values for the heat, from this latter cause alone, and displaces the maximum ordinate of the heat-curve toward the lower or ultra-red end. Dr. Müller (Poggendorff's Ann. CV.), indeed gives a construction showing how we may, from the incorrect curve of the prism-spectrum, obtain such as a grating would give could we use one; but he despairs of being able to get measurable heat from the grating itself, whose spectra are so much weaker than that from the prism, while even the latter are very hard to measure with any exactness by the pile.

No one, so far as I know, has hitherto succeeded in measuring the heat from a diffraction grating except in the gross, or by concentrating, for instance, like Draper, the whole upper half and the whole lower half of its spectrum upon the pile, and thus reaching some results, not without value, even as thus obtained, but of quite other value than those which may be expected when we become able to measure with close approximation the separate energy of each wave-length.

I have tried at intervals for the past four years to do this, and having long familiarity with the many precautions to be used in delicate measures with the thermopile, and a variety of specially sensitive piles,



had flattered myself with the hope of succeeding better than my predecessors. I found, however, that though I got results, they were too obscure to be of any great value, and that science possessed no instrument which could deal successfully with quantities of radiant heat so minute.

I have entered into these preliminary remarks as an explanation of the necessity for such an instrument as that which I have called the Bolometer (*βολή, μέτρον*), or Actinic Balance, to the cost of whose experimental construction I have meant to devote the sum the Rumford Committee did me the honor of proposing that the Academy should appropriate.

Impelled by the pressure of this actual necessity, I therefore tried to invent something more sensitive than the thermopile, which should be at the same time equally accurate, — which should, I mean, be essentially a “meter” and not a mere *indicator* of the presence of feeble radiation. This distinction is a radical one. It is not difficult to make an instrument far more sensitive to radiation than the present, if it is for use as an indicator only; but what the physicist wants, and what I have consumed nearly a year of experiment in trying to supply, is something more than an indicator, — a *measurer* of radiant energy.

The earliest design was to have two strips of thin metal, virtually forming arms of a Wheatstone's Bridge, placed side by side in as nearly as possible identical conditions as to environment, of which one could be exposed at pleasure to the source of radiation. As it was warmed by this radiation and its electric resistance proportionally increased over that of the other, this increased resistance to the flow of the current from a battery would be measured (by the disturbance of the equality of the “bridge” currents) by means of a galvanometer.

In order to test the feasibility of this method, various experiments were made. To secure a radiating body which will not vary from one experiment to another, or from day to day, is no easy matter. The source employed during the preliminary trials has been commonly the flame of a petroleum lamp within a glass chimney, the radiation being limited by a circular opening of 1 cm. diameter in a triple cardboard screen.\* In these first trials a single thin metallic strip, being stretched between appropriate metal clamps connected with the bridge by coarse insulated wires, was enclosed in a cylindrical wooden case, which being

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\* Very special precaution must be taken to prevent the screen itself from getting heated.

pointed to the aperture in the screen could be opened or closed at pleasure, and the resistance of the strip measured, as it varied through the effect of the radiant heat. In this way were examined various metals such as gold-foil, platinum-foil and various grades of platinum-wire, including some  $\frac{1}{1000}$  cm. in thickness; gold-leaf gummed on glass; extremely thin sheet-iron, both blackened with camphor-smoke and without such treatment, etc. The lamp-black augmented the heat registered, but, if too thick, produced anomalies of its own, due to its hygroscopic properties, which doubtless exist when it is used on the thermopile, but are not so obvious there. For example, the warm breath on such a lamp-blackened strip gave the indication of *cold* at the first moment, possibly owing to the *decreased* resistance from absorbed moisture.

Metals deposited on films of glass are found not to answer our purpose, because of the great amount of heat conducted away by the glass, however thin.

The requirements include, as was seen both from these preliminary trials and from obvious theoretical considerations, considerable electric resistance, great change of that resistance by temperature, lamina-bility, sufficient tenacity in the thin metal to enable it to support its own weight, and freedom from oxidation.

Iron would fulfil these conditions very well except the last, but it is liable to rust. This tendency can be partly overcome by the application of a thin coat of oil. Gold-leaf produced by the ordinary gold-beater's process lacks continuity, being filled with minute rents, and other metals are disqualified by other objections, such for instance as low melting-points. That the temperature of metallic strips of the thickness used may be very high, in spite of their great radiating surface and even when the battery is feeble, is seen from such an example as the following:—

An iron strip 7 mm. long, 0.088 mm. broad, 0.003 mm. thick, having the resistance of about  $2\frac{3}{4}$  ohms, was subjected to a current of about 0.6 Weber which had before produced a uniform cherry-red glow throughout the same length of platinum wire  $\frac{1}{100}$  cm. thick. The iron glowed more brightly, but only for about 2 mm. at the centre, and was melted at that point in about five seconds.

A number of experiments were tried to determine the proper excess of temperature of the strips used in the Bolometer over that of the surrounding case, for this excess (due to the heating by the battery current) must always exist; and the amount to give the best effect depends on many circumstances, and can only be determined by trial.

For instance, an iron strip 7 mm. long, 0.176 mm. wide, and 0.004 mm. thick, was made one arm of a Wheatstone's Bridge, and, with a battery of one gravity cell, the successive resistances of the strip were measured as its temperature altered, while the currents through it were made to vary by introducing definite resistances in the circuit. Then having the measured resistances of the strip, from the approximate formula  $t = \frac{R - r}{.004 r}$  (where  $R$  is resistance of iron at temperature  $t$  in Centigrade degrees,  $r$  the resistance at  $0^\circ$ ) we obtain the temperatures which are given below in the fourth column. The temperature of the room was  $27^\circ \text{C}$ .

Total Resistance in Circuit.	Absolute Current.	Resistance of Strip.	Temperature of Strip.
ohm.	Weber.	ohm.	$^\circ \text{C}$ .
279.4	0.0045	1.180	27.0
27.4	0.046	1.184	28.1
17.4	0.072	1.188	28.9
12.4	0.101	1.195	30.6
7.4	0.169	1.217	35.7
6.41	0.195	1.231	39.1
5.43	0.230	1.255	44.7
4.45	0.281	1.297	54.5
3.50	0.357	1.332	74.5
2.60	0.481	1.616	129.3

We see from the above that, when the temperature of the strip is raised very little above its surroundings, a change of one-hundredth Weber in the absolute current will raise its temperature less than half a degree; but that when it is raised more than two or three degrees above the surrounding temperature by the current, such a small increase of that current is accompanied by a greater rise in the temperature of the strip, and when the temperature of the strip is considerable, though not excessive, the same change of .01 Weber will raise this temperature by eight or ten times the former quantity; and hence (as it is important to notice) strong currents, and consequent high temperature in the strip, though giving larger galvanometer deflections, involve a yet greater increase of the probable-error of an observation on the galvanometer, caused apparently by air-currents about the heated strip.

A number of experiments with a similar iron strip (resistance 0.9 ohm) in a Wheatstone's Bridge (whose other arms were 0.9, 0.4, and 0.4 ohms) showed that with a half-ohm galvanometer a deflection of about 204 divisions could be obtained by exposure to lamp radiation as before described. The total current was 0.58 Weber; and, as one division of the galvanometer scale corresponded to about .000 0002

Weber, the differential current was .0000408 Weber, which allowing an increase of .004 in resistance for each added degree of temperature indicates\* that the strip had been heated somewhat less than  $0^{\circ} 15$  c. by the lamp radiation. A small (spherical-bulb) mercury thermometer placed at the same point rose six times this amount. Evidently only a small portion of the energy conveyed to the strip is retained as increased temperature. The immensely greater part is lost by re-radiation, conduction, and convection. This happens to the mercury thermometer to a very much smaller extent, since the comparatively slow conveyance of heat between its outer and inner layers enables it to retain a larger amount.

The conduction from front to back of the thin strip is practically instantaneous, and the equilibrium between heat received and heat radiated is so soon established that the effect upon the galvanometer is not increased perceptibly by prolonging the exposure after the needle has reached the end of its swing. Hence the time of exposure will, in general, be regulated by the sensitiveness of the galvanometer, and will very rarely exceed eight to ten seconds. The strip itself takes up and parts with (sensibly) all its heat in a fraction of *one* second.

This promptness in the action of the metal strip gives it a great advantage over the thermopile for measures of precision. But, beside this, the deflection produced by the single strip and bridge is greater than that from the thermopile, if the element of time enter into the comparison, and still more if the relative areas exposed to radiation be considered.

Although (for the reasons just cited) far from as sensitive as we can make it, such a strip then is yet more sensitive than the pile. A number of thermopiles, selected as the most sensitive in the writer's collection, have been exposed to the same source of radiation, placed at the same distance as in the previous experiments. They were directly connected with the unshunted galvanometer and enclosed in various cases, as follows:—

A. Large thermopile, by Elliott (Tyndall-lecture pattern), composed of sixty-three couples, on customary stand, but without cones. Face blackened. Area of working face = 15 mm. by 16 mm. = 240 sq. mm. Internal resistance 5.96 ohms.

B. Very sensitive thermopile of extra small elements (16 couples) with cardboard diaphragm aperture 6.6 mm. diameter. Area of working face (circle 6.6 mm. diameter) = 34 sq. mm. Internal resistance 0.97 ohm.

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\* See Formula, page 355.

*C.* Delicate linear thermopile (7 couples). Working face about 1 mm. by 10 mm. = 10 sq. mm. Internal resistance 0.72 ohm.

*S.* The iron strip, which was about 7 mm. by .176 mm. and whose working face was therefore about 1 sq. mm. Internal resistance 0.9 ohm.

The time of exposure was about five seconds for the thermopiles, and about one half this for the strip, the latter time corresponding to the rapid swing of the (designedly) insensitive galvanometer.

In the table, the first column gives the name of instrument; the second, the cross-section of the beam of radiant heat which is received upon it; the third is the actual deflection in galvanometer divisions; and the fourth the deflection for each square millimetre of exposed surface. The fourth column then (since the radiant energy falling on the broad pile could obviously be concentrated on the narrow strip with but little loss) gives approximately the relative sensitiveness of these instruments, using the same galvanometer ( $R = .5$  ohm) without considering the element of time: if that be considered, the relative sensitiveness of the strip will be still greater.

Instrument.	Area.	Deflection.	Sensitiveness.
	sq. mm.	div.	
A	240	211	.9
B	34	125	3.7
C	10	147	14.7
S	1	204	204.0

The total current employed with the last was about .58 Weber, of which one half passed through the strip, and this is somewhat greater than can be advantageously used in actual work. To increase the efficiency of the strip, another method is used in practice, which will be described immediately; but these numbers give only a rough comparison of the efficiency of the two instruments under similar circumstances.

Instead of a narrow metal strip, we might use one as broad as it is long, or, if we desired to increase the resistance while exposing the same area, we could cut this, for example, into ten narrow strips standing side by side, but only joined at their alternate ends, the electric current being passed through the members of the series successively. The single square strip, possessing  $\frac{1}{10}$  of the resistance of ten narrow ones taken in sequence, could be used with a low-resistance galvanometer and a battery, arranged for "quantity," transmitting a much larger

current; and if there were no limit to the current which could be advantageously used, other than that of the inconvenience of a large battery, this method might perhaps be practically advisable, as it certainly is the simplest. But the heating of the thin metallic strips by the current itself, imposes the necessity of keeping the latter below a certain maximum value. Employing always this greatest allowable current, a greater effect\* will be produced with the ten narrow strips than with the one broad one (using a galvanometer of much greater resistance than that used with the single broad strip). This subdivision of the metal has greatly increased the mechanical difficulties of construction, and I have felt that to make the apparatus generally useful I must learn how to overcome these difficulties, so that it can be produced at a not too great cost for ordinary use by the scientific student. It would at any time also, I repeat, have been easy to make a far more *sensitive* instrument than I am about to describe; but, from the first, my chief aim has been to produce one trustworthy, in the sense that it gives exact quantitative results.

After nearly a year's labor (I began these researches systematically in December, 1879), I have procured a trustworthy instrument. It aims, as will have been inferred from the preceding remarks, to use the radiant energy, not to develop force directly as in the case of the pile, but indirectly, by causing the feeble energy of the ray to modulate the distribution of power from a practically unlimited source.

To do this I roll † steel, platinum, or palladium into sheets of from  $\frac{1}{16}$  to  $\frac{1}{8}$  of a millimetre thickness; cut from these sheets strips one millimetre wide and one centimetre long, or less; and unite these strips so that the current from a battery of one or more Daniell's cells passes through them. The strips are in two systems, arranged somewhat like a grating; and the current divides, one half passing through each, each being virtually one of the arms of a Wheatstone's Bridge. The needle of a delicate galvanometer remains motionless when the two currents are equal. But when radiant heat (energy) falls on one of the systems of strips, and not on the other, the current passing through the first is

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\* We cannot say exactly how much greater, since our formulæ do not take account of the temperature as actually modified by re-radiation and conduction, but only of the amount of heat imparted.

† Experiments are now in progress with still thinner films of metal produced by electrical or by chemical deposition. I have had the good fortune in experiments now making in this direction, to secure the aid of Professor A. W. Wright of Yale College, and of Mr. Outerbridge of the United States Mint at Philadelphia.



diminished by the increased resistance; and, the other current remaining unaltered, the needle is deflected by a force due to the battery directly, and mediately to the feeble radiant heat, which, by warming the strips by so little as  $\frac{1}{10000}$  of a degree Centigrade, is found to produce a measurable deflection. A change in their temperature of  $\frac{1}{100000}$  degree can, I believe, be thus noted; and it is evident that from the excessive thinness of the strips (in English measure from  $\frac{1}{2000}$  to  $\frac{1}{15000}$  inches thick) they take up and part with the heat almost instantly. The instrument is thus far more prompt than the thermopile; and it is also, I believe, more accurate, as under favorable circumstances the probable error of a *single* measure with it is less than one per cent. When the galvanometer is adjusted to extreme instability, the probable error of course is larger; but I have repeated a number of Melloni's measurements with the former result.

I call the instrument provisionally the "Bolometer," or "Actinic Balance," because it measures radiations and acts by the method of the "bridge" or "balance," there being always two arms, usually in juxtaposition, and exposed alike to every similar change of temperature arising from surrounding objects, air-currents, etc., so that the needle is (in theory at least) only affected when radiant heat, from which one balance-arm is shielded, falls on the other.

Its action, then, bears a close analogy to that of the chemist's balance, than which it is less accurate, but far more sensitive. The sensitiveness of the instrument depends, as has been explained, upon the amount of current used. With the current which experience has recommended, as leaving a very steady galvanometer needle, this sensitiveness appears to be from ten to thirty times that of my most delicate thermopiles, area for area; but I consider this quality valuable, only in connection with its trustworthiness as a *measurer*, always repeating the same indications under like conditions.

The working face of the instrument, as I have used it, exposes about one half of one square centimetre to the source of radiant heat (it can easily be made of any other size, larger or smaller); and the strips are shielded from extraneous radiations by the most efficient precautions which a rather long and painful experience in guarding against them has taught me.

#### DESCRIPTION OF FIGURE 1.

There are two disks of hard rubber, each 30 mm. in diameter and 3 mm. thick in the thickest part. Each has a concentric opening 8 mm. square. The first has four hollow brass cylinders, *a*, *c*, *b*, *d*, and the



second four corresponding holes in the ebonite,  $a', c', b', d'$ . When these cylinders are in the holes they act as steady-pins. In the part  $a c b d$  are eight parallel channels, each about  $\frac{1}{2}$  mm. wide and 1 mm. deep, symmetrically disposed across the square. The seven ridges between these channels are each rather narrower than the channels, so that the whole width from outside to outside is a little less than 8 mm. On the part of  $a' b' c' d'$  corresponding are seven similar channels, the centre one being in the centre of the square. On each side of the square in  $a b c d$  are four similar channels, and on each side of that in  $a' b' c' d'$  are three channels. When the two disks are put together (one may be supposed to revolve like the lid of a box about the imaginary hinge  $XY$ ), the ridges on one fall into the channels of the other. At  $e, f, g, h$ , are split pins of platinum, and at  $e', f', g', h'$ , corresponding hollow cylinders of platinum to receive them.

The current enters by the brass of the hollow steady-pin,  $a$ , and passes eight times across the square as shown, then crosses over through the pin  $e$  to  $e'$ , passes seven times across the square, back by  $h' h$  to the first disk and then out by the pin  $b$ . Where the current crosses the square, it is conducted by strips of iron, each a little less than 0.5 mm. wide and about 0.004 mm. thick, laid in the channels. There are therefore, when the disks are put together, fifteen of these strips drawn parallel across the square, each at the bottom of its channel, of which eight lie in one plane in the first disk and seven in another plane in the second disk, the two planes being about 1 mm. apart when the disks are fitted together. The strips in each set lie opposite the openings between the strips of the other set. The other current enters at  $c$ , goes along four iron strips, up the pin  $f$  to  $f'$ , then three times along iron strips, then round to the other side of disk *number two*, then three times along iron strips, then down a copper wire to  $g'$ , then through  $g$  back to disk *number one*, then four times along iron strips and out at  $d$ . There are therefore twenty-nine strips disposed in two circuits,\* fifteen in the central circuit (these fifteen form virtually one arm of the bridge), and fourteen in another circuit which surrounds the former. These fourteen, disposed in two groups for symmetry, form then the second arms. Every joint is soldered.

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\* These strips are preferably not soldered, but continuous, being struck by a punch from a single film of metal. The number of these and their size is varied in different instruments, which may be adapted to a low or a high resistance galvanometer. The slight difference of resistance between the central and side strips it is intended to make up by resistances introduced within the balance-case, so that the use of a resistance box will not be necessary.

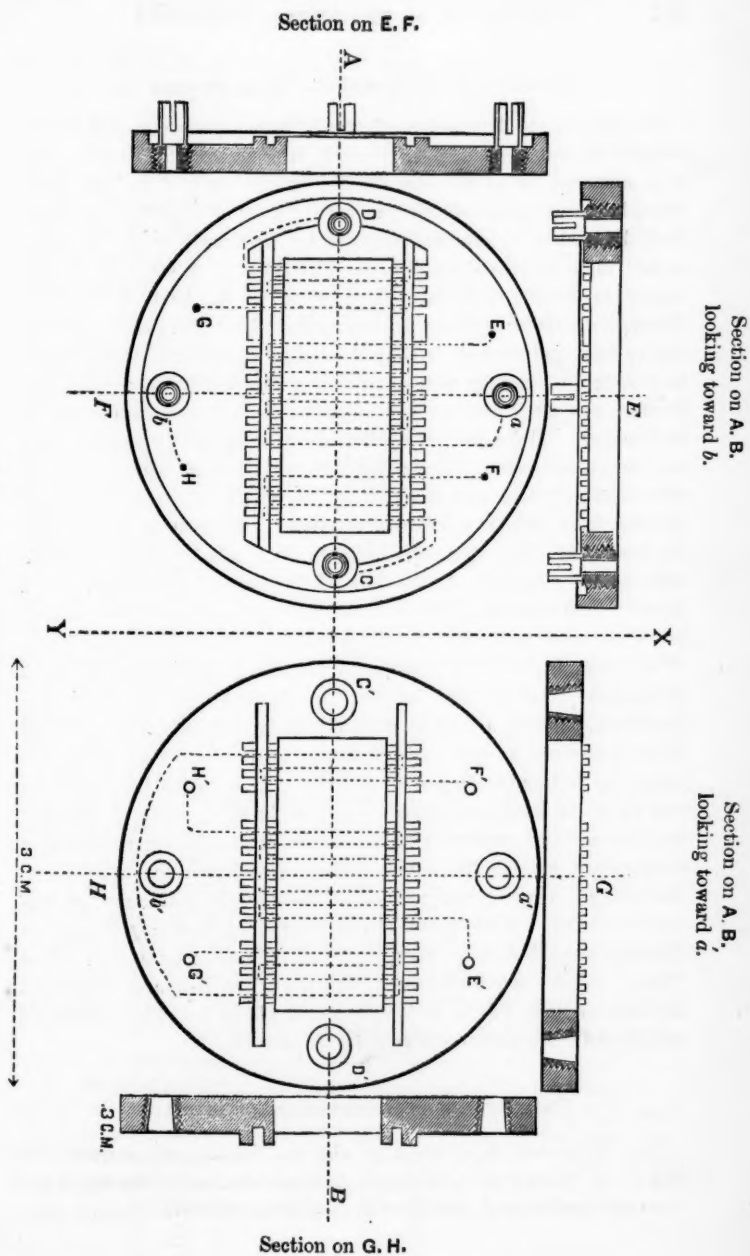


FIG. 1. THE BOLOMETER.

Scale: Twice full size.

## DESCRIPTION OF BALANCE CASE, FIGURE 2.

To protect the Bolometer effectually from air-currents and sudden changes of temperature, and to enable it to be handled more easily, it is enclosed in a chamber situated in the axis of a long cylindrical holder of non-conducting material (wood or ebonite), which can itself be held by a suitable clamp pointed accurately in any direction or laid in a horizontal position on *Ys*. This chamber is lined with copper, to secure an equable distribution in the heat of its walls. Through a circular opening, 15 mm. wide in front, the grating of strips can be seen, and over all is slipped a hollow cylindrical cover of wood or ebonite 15 cm. long, within which is a second tube containing four or more concentric cardboard diaphragms pierced by apertures 6 mm. in diameter. These disks of cardboard are separated by ebonite rings, and form a succession of drum-like chambers, through whose apertures the radiation passes unobstructed, but by which the entrance of air-currents from without is effectually stopped. In front of all, a revolving cardboard diaphragm with suitable stops admits or shuts out the radiation at pleasure. At the back of the copper-lined chamber is a layer of solid non-conducting material, through which pass the connecting wires, terminating in metal plugs insulated from the copper lining. With these plugs the four terminals of the double grating are connected by clamping-screws. The Balance Case is prolonged yet 15 cm. farther back, forming a tube in which may be included and protected from air-currents an adjustable resistance or rheostat by which the two arms may be brought to perfect equality. It is advisable to have the two halves as nearly as possible equal at the first; since, if unequal, the increment of resistance in the larger, caused by a general rise of temperature, exceeds the corresponding increment in the smaller, necessitating a frequent readjustment of the variable resistance and producing a "drift" in the galvanometer needle, which slowly changes its direction according as the temperature of the room rises or falls. This "drift" is not a peculiarity due to the use of the Bolometer, however, as a similar drift, due to different causes, affects the galvanometer (if equally delicate) when used with the thermopile.

## DESCRIPTION OF CONNECTIONS, FIGURE 3.

The Bolometer, *A*, is connected with the distant coils, forming the rest of the Wheatstone's Bridge, by four insulated copper wires, *u, v, y, z* (twisted together and covered with flannel to reduce the effect of vary-

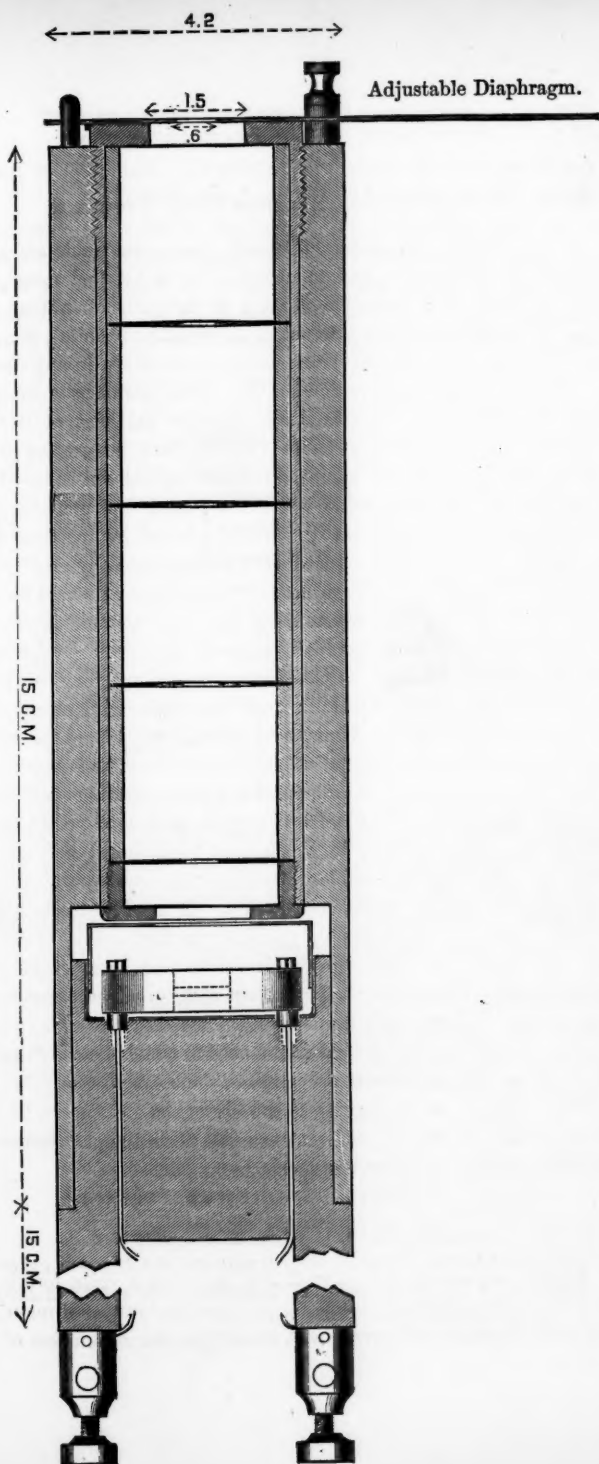


FIG. 2. SECTION OF BOLOMETER CASE AND BOLOMETER.  
Full size.

ing temperature in these to a minimum). The binding posts, etc., should also be protected against temperature changes.

In order to prevent gross variations in the electric current from variations in the battery, which might vitiate the results slightly by affecting the differential current, there is introduced in the circuit leading to the Wheatstone's Bridge,  $W$ , a shunted galvanometer,  $g$ , whose deflection indicates the amount of current passing through the

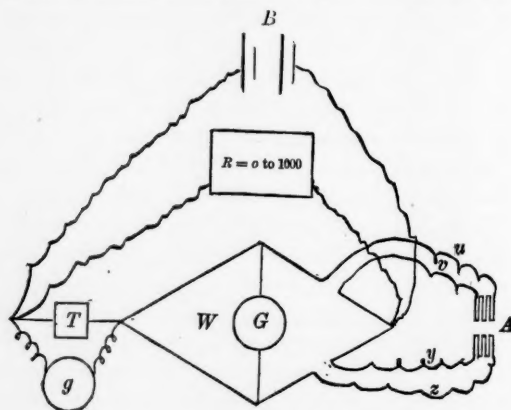


FIGURE 3.

latter. This can be varied within certain limits by altering the resistance of a battery shunt,  $R$  (see Fig. 3). Knowing this current, we can easily compute the differential current flowing through the sensitive "bridge" galvanometer, for any given change in either arm of the bridge, by using the following approximate formula:—

Designating by  $a$  Resistance of one arm of Wheatstone's Bridge.  
 "  $na$  " other " "  
 ( $n$  being in practice very slightly greater than unity.)  
 "  $x$  Resistance of each of the other arms.  
 "  $g$  " galvanometer.  
 "  $b$  " one cell of battery (resistance of line wire neglected).  
 "  $E$  The electromotive force of one cell.  
 "  $c$  " differential current.

We find for the value of the current produced in the galvanometer through the bridge, in terms of the whole current  $C$  (making  $n = 1$  in the denominator),—

$$c = \frac{(n-1)ax}{2(2ax + ga + gx)} Q.$$

But

$$C = \frac{2E}{2b + a + x}$$

$$\therefore c = \frac{(n-1)ax}{(2ax + ga + gx)(2b + a + x)} E.$$

It is desirable to get a rough idea of the relation between work derived directly from the energy in a given ray (as of sunlight), and that coming mediately, through the effect upon the battery current modified by the balance. A sunbeam one square centimetre in section, which will, under the ordinary Allegheny sky, warm 1 gramme of water  $1^\circ$  C. in 1 minute or  $\frac{1}{60}^\circ$  in 1 second, will raise the temperature of a sheet of water 1 mm. by 10 mm., or  $\frac{1}{10}$  of a square centimetre in area and  $\frac{1}{800}$  mm. thick,  $83\frac{1}{3}^\circ$  C. in 1 second, if all the heat be retained; and, since the specific heat of platinum is .032, the same sunbeam will raise a corresponding strip of platinum  $2,603^\circ$  C. in 1 second, it being supposed here that there is no loss of heat by re-radiation, conduction, or convection. This gives the startling result that the heat received from ordinary sunshine on such a platinum strip would be sufficient to *melt* it in less than a second, if it could all be retained, and is an independent testimony to the rapidity with which these thin strips take up and part with their heat, and to the promptness of action of the balance, whose actual temperature is raised but a very few degrees by this radiation.\*

The heat produced in a strip of the above description by a current of  $\frac{1}{10}$  Weber is found to be (using C. G. S. notation),—

$$\frac{(.01^2) \times .5 \times 10^9}{4.2 \times 10^7} = .00119 \text{ gramme degree per second,}$$

capable of raising the temperature of the strip  $1,866^\circ$  C. in 1 second *if all retained*. A current of  $\frac{1}{10}$  Weber raised a narrower *iron* strip  $12^\circ.8$  C. (see Table, p. 345). As in the first example it may be shown by calculation that only a small fraction, in this case about  $\frac{1}{230}$  of the heat developed, is retained.

It is intended eventually to enclose the Balance in a vacuum, and to study more closely the losses by radiation which occur in it, apart from

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\* The resistance of one arm of an Actinic Balance, exposed to radiation from the sun at an altitude of  $50^\circ$  with an ordinary blue sky, was increased by an amount which indicated that its temperature had been raised by  $7^\circ$  C. By calculation it was found that the energy in the sunbeam would have been sufficient *if all had been retained* to heat the strips in 1 second about 450 times this amount.

the losses produced by conduction and convection, which in a very perfect vacuum are practically negligible; for the conduction through the metallic connections of the strips themselves is wholly insignificant, owing to the excessively small cross-section of the latter in proportion to their length. With the value of the loss by radiation thus obtained, the above results, which are of course presented only as a first approximation, can be corrected.

The preceding remarks comprise what is most essential in a description of the working apparatus founded on the method of changed electric resistance.

I write far from large libraries, and do not pretend to give the bibliography of the method, if it have one. The only notices of a use of the principle involved in this instrument that are known to me are the following:—

1. On the Measurement of Resistance to the Conduction of Electric Currents, and on a Galvanic Differential Thermometer, by A. F. Svanberg. Poggendorff's *Annalen*, 1851, vol. lxxxiv. p. 411.

2. On Measuring Temperatures by Electricity, by C. W. Siemens. *Proceedings of the Royal Institution of Great Britain*, March 1, 1872, vol. vi. p. 438.

Mr. Siemens has made subsequent special applications of this principle.

This paper, as a description of the apparatus for measuring radiant energy, ends here; but I may mention the following results which have been obtained with the instrument in other researches, to give a more just idea of its efficiency as a working-tool for the physicist.

In illustration of the work which the balance may be used for, take the following repetition of one of Melloni's experiments.

Source of heat, petroleum lamps (argand burner with glass chimney) at 15 cm. distance. Radiation limited by screen with 1 cm. circular aperture at 10 cm. from the steel Balance.

The unimpeded radiation was compared with that transmitted by distilled water and by an aqueous solution containing ten per cent (by weight) of common alum. The liquids were contained in a glass cell (sides 2.5 mm. thick, distance between sides 19.0 mm.). Temperature 21° C. Galvanometer not sensitive.

Deflection (mean of five trials) —

by radiation through distilled water and glass	= 16.5 div. }
"    unimpeded	= 107.6 " }
"    through 10% alum solution and glass	= 13.7 " }
"    unimpeded	= 103.8 " }



## Percentage of radiation transmitted —

by distilled water	= 15.3
„ 10% alum solution	= 13.2

The following galvanometer readings for “lamp radiation” (as just described) are given in full to show the method of procedure, and also the liability to variation in successive exposures when great instrumental sensitiveness is not required:—

Before exposure, stationary at	Exposed, settled at	Exposure ceasing, returned to	Deflection.
div. —24	div. +106	div. —24	div. +130
—24	+105	—26	+130
—27	+102	—29	+130
—29	+100	—29	+129
—29	+101	—29	+130
Mean = + 129.8			

This is given as a fair sample of the average error on such work as is involved in most of Melloni's experiments; where great sensitiveness in the galvanometer (according to the modern standard of what constitutes sensitiveness) is not required.

The first measures, on nearly homogeneous rays in the *diffraction* (reflection) spectrum, ever taken by any one that I know of, were taken by this instrument on Oct. 7, 1880, used with an extremely delicate reflecting galvanometer by Elliot, of about 20 ohms resistance and a reflecting grating on speculum metal by Mr. Rutherford of 681 lines to the millimetre. Measures have been taken every fair day since, the source of energy being the sun.

The rays from a slit five metres from the grating fell directly on it (without any collimator); these were, after diffraction, received on a silvered glass mirror, and this formed an image of the first spectrum about 20 centimetres long (from  $\lambda = .0004$  to  $\lambda = .0007$ ) and 8 mm. wide. The “Balance” then, whose acting face is only about  $\frac{1}{30}$  the length of the visible spectrum, and less than  $\frac{1}{100}$  the length within which energy is found in a degree sufficient for it to measure, receives nearly homogeneous rays (which have passed through no absorbing medium whatever except the solar and terrestrial atmospheres), and this extremely minute amount of heat is found to give a galvanometer deflection of some hundred divisions, where thermopiles have hitherto failed to register any (on homogeneous rays).

The corrections for minute selective absorption in speculum metal and silver reflections, and in the metal of Balance strips, are still to be

applied. The rough galvanometer deflections for different wave-lengths are, where the slit used is so narrow as to give all the principal Fraunhofer lines sharply on the screen, as follows. (In corresponding curves, wave-lengths are abscissae; reduced mean galvanometer deflections, ordinates.)

	mm.							
$\lambda =$	.00035	.0004	.0005	.0006	.0007	.0008	.0009	.0010 .0011
	div.							
Defl.	12	55	207	246	198	129	80	58 41

The corrections for the underlying second and third spectra not being fully applied, it can only be said that these values are trustworthy (as first, approximations) as far as from .00035 mm. to .0007 mm. The values below .0007 which give the sum of first, second, and third spectra are, perhaps, too large. They are hitherto unpublished, and they at least, though as yet approximative, show that the *heat maximum in a normal spectrum is not in the ultra-red, but is at least as far up the spectrum as the orange near D*; and this result may be relied on, any smaller values below  $\lambda = .0007$ , as well as all favorable atmospheric circumstances (high sun, blue sky, etc.), rather tending to move it toward the violet.

These measures show a certain approximation of the "heat" curve to the "light" curve, though these are commonly drawn with their maxima in entirely different parts of the spectrum. Viewing the actual distribution of energy here, and then comparing it with the so-called "heat," "light" and "actinic" curves of the text-books, we have evidences, I think, of interesting results already reached by this instrument, and which have been possible only by its use. Among these, we observe that (contrary to the statements of our text-books, and contrary, as I think, to most present scientific opinion) the great proportion of all solar heat received at the earth's surface does *not* apparently lie in the non-luminous parts of the spectrum. Not only is the heat maximum in the luminous part, but the total sum of non-luminous heat (as far at least as our measures extend) is relatively small, the joint effects of ultra red and ultra violet radiations (so far as measured) not making up the sum of those in the visible portion. This is a result to me unexpected, but which I think may be relied on; and it is, if true, sufficiently important to make me hope that the society will feel that the instrument whose construction they have promoted is already of utility.

The above illustrations form parts of other researches, and are borrowed for this paper merely to show the action of the instrument, and to enable each reader to judge for himself of its value as a *measurer* of radiations.

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## XIX.

ON THE USE OF THE ELECTRIC TELEGRAPH DURING  
TOTAL SOLAR ECLIPSES.

BY D. P. TODD, M.A.

Presented January 12, 1881.

ONE of the most intractable considerations in the study of the sun and its surroundings lies in the small amount of time which is available for the prosecution of that study. Most of the phenomena in the neighborhood of the sun can be investigated only when the sun itself is hidden during eclipse. If we suppose a single observer to be prepared for the observation of all the total solar eclipses of a century, we shall find that the entire amount of time during which he may contemplate the totally eclipsed sun will not differ much from an hour. We may be sure, then, of the expediency of any scheme whereby the rare moments of these eclipses may be utilized to their utmost extent. If such scheme is devised, two important results are like to follow:—

- (1) Economy of the sum-total of energy in any particular line of solar research.
- (2) A consequent enlargement of the means of research in other directions.

The general conception of the scheme proposed in this paper may be very briefly stated: Suppose a station to the east and a station to the west on the line of any total eclipse, as widely separate as practicable, and equipped for similar observations of discovery during the progress of the eclipse: the method proposes the electro-telegraphic transmission of important observations made at the western station to observers at the eastern station, with due speed for their verification or rejection when the lunar shadow reaches the latter station.

For illustration, consider the next total eclipse, — that of 1882, May 16. In detail, the particular advantages in connection with this eclipse seem to be about these:—

(1) The path of totality is almost exclusively on land. Central eclipse begins in West Africa; the line of totality passes to the north-east, crossing Upper Egypt, and the Nile at El-Akhmym; thence over the Red Sea, crossing the Tigris a few miles to the south of Bagdad; then passing a little to the south of Teheran, it traverses Central Asia, and leaves the Asiatic continent somewhat to the north of Shanghai.

(2) Though not generally through the inhabited regions of the globe, the path of totality lies through several inhabited regions which are widely separate; viz., Egypt near the Nile, Central Persia, and Eastern China.

(3) These regions are inter-connected by telegraphic cables and land-lines. From El-Akhmym a land-line runs to the north along the banks of the Nile, and thence to Diarbekir and Constantinople,—from either of which Teheran, the capital of Persia, is readily accessible by telegraph. From Teheran, a land-line runs southeast through Persia, Beluchistan, and Hindostan to Madras; and from thence cable-lines extend through Singapore and Hong-Kong to Shanghai. An additional advantage attaches to this eclipse-line from there being a duplicate line of connection by telegraph between El-Akhmym and Shanghai: it would be advisable that any message of discovery at the former station should be repeated over this duplicate line,—from Constantinople, to Vienna, to Warsaw, to Moscow, and thence through the Russian overland line extending across Siberia to Wladiwostok, to Nagasaki, and Shanghai. The through-transmission of the message might then be secured beyond doubt.

Now, we will suppose that an important observation of discovery is made at El-Akhmym,—an observation of an intramercorial planet, for example. Between forty and forty-five minutes of absolute time elapse before totality comes on at Teheran. During this interval, the observer at El-Akhmym will have an abundance of time for transcribing the apparent magnitude and the precise position of the new body, and transmitting the same to his fellow-observer at Teheran several minutes before the lunar shadow reaches him. The latter observer will then have leisure to proceed with the setting of his circles, the verification of their readings, and the pointing of his instrument to the precise part of the heavens indicated. He may then be able to see the suspected object before the eclipse becomes total. He may also decide upon a neighboring star for comparison with the planet, and thus obtain a very accurate determination of its position. The observer at Teheran should also be prepared for an independent

search for the suspected planet, in the event of receiving a negative message from the observer at El-Akhmym.

The observation at El-Akhmym should also be transmitted to Shanghai (reached by the shadow more than two hours after totality at Teheran), for independent verification at that point. We might thus observe the result of nearly three hours' motion of the planet,—which we might reasonably expect to give important data in regard to its orbit about the sun. Of course, the result of the observations at Teheran would also be transmitted to the observer at Shanghai.

It was my intention, primarily, to have considered the total eclipse of 1882 merely as an illustration of the method proposed. Further investigation, however, seems to show that it is at least one of the two most favorable eclipses during the present decade, if not during the present century. A few additional considerations merit attention:—

(1) Accessibility of the observing-stations. El-Akhmym, on the Nile, is only two or three days from Cairo, and nearly the whole journey may be made by rail. By steamer on the Nile, the journey is something like two days longer. Teheran, in so far as I have been able to ascertain, is not difficult of access, though most of the journey must be by caravan-routes, and very little by rail. Of the accessibility of Shanghai, nothing need be said.

(2) Some doubt may exist with regard to the possibility of telegraphic transmission with sufficient celerity, owing to the necessary number of repetitions of the messages. As for the lines from Egypt to Teheran, and from Egypt to China, the matter will seem less embarrassed from the fact that these lines are largely under the same control. Three quarters of an hour seems an abundance of time for the transmission of an imperative message from Egypt to Shanghai, allowing five or six repetitions of the message on the way. Of course, the success of the scheme will rest largely with the thoroughness of preconcerted arrangement. The generous courtesy hitherto shown astronomers by the officials in charge of telegraphic lines encourages the belief that they would be disposed to do everything in their power on such an occasion.

(3) The cloudiness of the stations. The chances of clear weather in Upper Egypt in the middle of May appear to be very good. I have pleasure in thanking Mr. Cleveland Abbe, of the office of the Chief Signal Officer of the Army, for his references in this matter. From observations at Alexandria in the month of May, of the years 1870-74, the following results are obtained:—

Mean cloudiness, 1.7.

Number of rainy days, one in five years.

Number of totally cloudy days, one in five years.

Number of wholly clear days, 21 each May.

Up the Nile, as far as El-Akhmym, the conditions would be a little less favorable. With Bagdad and Teheran in the month of May, the case stands very similar.

There are no readily available records with regard to the cloudiness of Shanghai.

(4) The duration of totality of the eclipse of 1882 is not very favorable. At El-Akhmym totality lasts one minute and twelve seconds. At Teheran the eclipse is total something like one minute and two tenths. And at a point a few miles to the north of Shanghai, the duration of totality is nearly half a minute; but this short interval would suffice for the purpose of verification simply.

We may examine the conditions of applicability of the telegraphic method to total eclipses subsequent to that of 1882:—

*a.*—The total eclipse of 1883, May 6. The path of totality lies almost entirely on water, beginning to the east of Australia, and going between New Caledonia and New Zealand, and leaving the earth to the west of South America. In the longitude of the Marquesas Islands, the duration of totality is about five minutes and fifty seconds, but there is no other station where the eclipse will be observable on land.

*b.*—The total eclipse of 1885, September 8. In the longitude of Wellington, New Zealand (the south point of the north island), the duration of totality is one minute and fifty-four seconds. It does not appear, however, that telegraphic communication with any other station will be practicable.

*c.*—The total eclipse of 1886, August 29. Here again we have an ocean-track except for a few miles at the beginning, and a small portion at the end. In Grenada the duration of totality is three minutes and fifteen seconds; on the Atlantic Ocean, off the coast of Liberia, six minutes and thirty seconds; and on the western coast of Africa (latitude  $12^{\circ}$  south), about four minutes and forty-five seconds. The time of the eclipse, however, is the storm-season in the West Indies; so that we are not warranted in expecting very much of this eclipse, notwithstanding the extraordinary duration of totality.

*d.*—The total eclipse of 1887, August 18. The totality-path of this eclipse begins in central Germany, and passes to the north of Moscow,

where the duration of totality is two minutes and thirty seconds. It then follows approximately the course of the Russian overland telegraphic line, and crosses Lake Baikal, where the duration of totality is three minutes and thirty-eight seconds. This eclipse will, therefore, be even more favorable than that of 1882 for the application of the telegraphic method.

*e.* — The total eclipse of 1889, December 22. The track of this eclipse is similar to that of 1886. At Bridgetown, Barbadoes, totality lasts one minute and forty-eight seconds. On the west coast of Africa (latitude  $10^{\circ}$  south), three minutes and thirty-four seconds. It seems probable that the method will not be applicable to this eclipse.

An acknowledgment is due the editor of the astronomical notes in *Nature* for the greater part of the data relating to the eclipses which I have cited.

WASHINGTON, January 8, 1881.



## XX.

## LARGE TELESCOPES.

BY EDWARD C. PICKERING.

Presented April 13, 1881.

THE small amount of work accomplished with large telescopes has often been the subject of unfavorable comment. This criticism applies with especial force to this country, where there are nearly a dozen telescopes having an aperture of a foot or over, besides two of the largest size now in course of construction, and two of 26 and 24 inches aperture which are unmounted and have been for several years perfectly useless. Among so many, it seems as if one might be spared for a trial of the following plan, which if successful would produce at a small expense far more work than could be obtained with a mounting of the usual form.

Suppose that the telescope is placed horizontally at right angles to the meridian, and that a plane reflector inclined to its axis by  $45^\circ$  is placed in front of it. This reflector may revolve around an axis coinciding with that of the telescope. Such a mounting has been used in transit instruments, and gives much satisfaction in the meridian photometer of the Harvard College Observatory. The principal difficulty with a large instrument would lie in the flexure of the reflector. This difficulty has, however, been overcome in a great measure in reflecting telescopes by various ingenious devices. In the present case, since the reflector rotates only around one axis instead of two, the problem is much simplified. A slight motion at right angles of perhaps  $5^\circ$  would be a great convenience, as will be shown below, and would probably be insufficient to materially affect the flexure. It may be said that it is more difficult to make a plane surface than one that is curved. But the principal effect of a slight curvature would be to change the focus of the telescope, the aberration being much less than the effect of the varying flexure. Let us admit, however, that the best definition cannot be obtained, in considering the purposes to which such an instrument could be applied without disadvantage.

Many advantages will be apparent on comparing such a mounting with an equatorial. Great steadiness would be secured, since the mirror would be the only portion moved, and this would be placed directly upon a low pier. Instead of a large and expensive dome which is moved with difficulty, the mirror would be protected by a small shed, of which the roof could be easily removed. It would, therefore, be opened and ready for use in a very short time, and would quickly take the temperature of the surrounding air. The object-glass would be mounted directly upon a second pier, and, as it would not be moved, would be in very little danger of accident. The tube could be made of tin or other inexpensive material, as its flexure is of no importance. It could easily be protected from the changes of the temperature so troublesome in the tube of a large equatorial. If preferred, it might even be exhausted of air, or filled with hydrogen, and the effect of the changes of temperature thus greatly reduced.

The eyepiece could be mounted on a third pier, and would be so far distant horizontally from the mirror and object-glass that there is no reason that it should not be enclosed in a room which may be warmed. The comfort in winter of working in a warm room will be appreciated by those who have used a large telescope in a cold climate. The result is sure to be an increased precision in the observations, and a possibility of prolonging them over longer intervals. A similar effect is produced by the constant direction of the line of sight. No especial observing chair is needed. There is no limit to the size of the attachments which may be made to the eyepiece, since they need not be moved. This is a great advantage in certain spectroscopic and photometric measurements. A strong wind interferes seriously with many observations, as it is impossible to make a telescope so stiff that it will not be shaken by sudden gusts. In the plan here proposed the mirror alone is exposed, and its surface is too small to give trouble.

By means of a long handle the position of the mirror may be regulated from the eye-end, and the declination of the object observed read by small telescopes. If the mirror can be moved at right angles to the meridian  $5^{\circ}$  from its central position, an object at the equator may be followed for forty minutes, and other objects for a longer period. Without this motion an object may be followed for three or four minutes by moving the eyepiece alone. Clockwork may be applied to the mirror, or less easily to the eyepiece. The focal length may be increased almost indefinitely if desired, and certain advantages will be thus attained in the diminution in the defects of the object-glass, although those of the reflector will not be affected. If the telescope is

to be erected at a great elevation the advantages of the present plan are at once apparent. Many nights of observation would be secured which otherwise would be lost owing to the wind and cold. The simplicity in the construction of the building would be a great advantage, as a large dome in so exposed a situation would be kept free from snow with much difficulty, and might be a source of danger in winter storms. If found impracticable to observe during the winter, it would be possible to have a duplicate mounting below, and remove the lens and mirror from one to the other.

It is evident that the saving of cost would be very great not only in the observatory building and dome, but in the tube, observing chair, clockwork, etc.

If a reflector could be constructed whose surface was the portion of a paraboloid whose abscissa equalled that of the focus, the instrument could be much simplified. No object-glass would then be required, the reflector taking the place both of mirror and lens. All the light intercepted by the objective would thus be saved, and but a single surface need be adjusted and corrected. With the advance in mechanical methods this does not seem wholly impracticable, especially with a mirror of long focus. Since the final correction must always be made by hand, it makes but little difference what is the exact form of the surface.

In any case it would be a great advantage that the mirror could be reground, repolished, or resilvered without moving it from its place. It would only be necessary to place it horizontally, and the grinding machinery could be kept permanently near it. If plane, the perfection of its form could also be tested at any time by setting it on edge, and viewing the image it reflected by a collimating eyepiece attached to the large telescope. Another method would be to place a heliotrope a few hundred yards to the north or south of it, and the light from this would form an excellent artificial star, available whenever the sun shone.

The greatest advantage is the rapidity with which observations could be made. No more time would be lost in identification than with a transit instrument, so that a large number of objects could be examined in the course of a single hour. Any one who has worked with a large telescope knows how much time is lost in opening and closing the dome and in finding and identifying minute objects.

Let us now consider to what purposes a large telescope mounted as suggested might be applied.

I. Sweeping. For the discovery of new objects this mounting presents especial advantages. It might be used for the detection of new

double stars, of nebulae, of red stars, or of objects having singular spectra, as planetary nebulae, banded stars, and variables of long period. Suppose that the field of view had a diameter of somewhat over one minute of time, and that a small motor was attached to the mirror which would move it uniformly over  $5^\circ$  in declination in this time, and then bring it quickly back to its first position. The observer would then have presented to him a series of zones  $5^\circ$  long and one minute wide. The sweeps should overlap by a small amount, so that the entire region could be covered in a single evening. The observer could have a few seconds rest between each zone, while the motion of the mirror was reversed. If an object of interest was suspected, it could be located by merely noting the time at which it was seen. The right ascension would be given directly, and the declination would be found by interpolation from the time of beginning and ending the sweep. An examination of the object and a determination of its exact location should be made on another evening.

II. Measures of position. For many purposes positions could be determined with this instrument as in a transit circle. It would generally be better, however, to make the measures differential, leaving the mirror at rest and observing the transits of the object to be determined and of two or more companion stars. The method of the ring micrometer might be employed, or some modification of that with inclined lines. In the latter case the zero of position could be found by the transit of preceding stars, by setting the reticule by a divided position circle, or perhaps better by keeping it in a fixed position, determining the direction of the lines once for all, and applying a correction for the declination of the object observed. Stars could be compared differing nearly a degree in declination, as the eyepiece could be moved without danger of disturbing the reticule. For the same reason the star could be followed for three or four minutes, and its transit over a great number of wires observed. It is here assumed that the distortion produced by the mirror is not very great. A slight distortion would do little harm, as it would be the same for all stars of equal brightness. If the stars differ greatly in brightness, the observer should determine his personal equation between them in any case, and the same operation would eliminate the effect of the distortion. The large aperture of the instrument would permit the observation of stars quite beyond the reach of any meridian circle. The faintest asteroids could thus be readily measured, and could probably be followed in many cases on successive evenings to their stationary points. Zones of stars could be observed very conveniently for the formation of charts or catalogues, for the discovery of asteroids, stars with large proper motion, etc.

Probably the definition could not be sufficiently good for the measurement of the closer double stars, but if clockwork was attached, faint companions could be measured or approximate positions of the coarser pairs determined very rapidly. The positions of nebulae could also be observed with a view to detecting their proper motion. Stars having a large proper motion might be observed, and the observations so arranged that any very large parallax would be detected. A similar search for a large parallax of variable stars, short-period binaries, minute planetary nebulae, or stars having singular spectra, might lead to interesting results. The argument that no ordinary star is very near does not apply to such objects.

III. Spectroscopy. The increased dimensions which could be given to the spectroscope, and its steadiness, would compensate in a great measure for a defect in definition. By Zöllner's reversion spectroscope the slit might be dispensed with, and also the necessity of clockwork. So many stars could be observed in a single evening that systematic errors could be in a great measure eliminated, and as the spectroscope would not be moved, we should have a great assurance that the deviations were real. Of the six thousand nebulae hitherto discovered we know nothing of the spectrum of more than three or four hundred, while the observation of all the others with a large horizontal telescope would not be a very formidable undertaking. It would also be interesting to observe the spectra of all the clusters. It is possible that some may consist of stars having singular spectra, or even of disconnected nebulous masses, in fact forming clusters of planetary nebulae. The interesting discovery by Dr. Copeland that Burnham's double nebula in Cygnus is gaseous, shows the same tendency to aggregation in these bodies as in stars. Observations of the spectra of all the red stars and variables would also probably lead to interesting results.

IV. Photometry. Should the instrument be devoted to photometry, numerous problems suggest themselves. Variable stars could be observed near their minimum when too faint to be identified with an equatorial without great loss of time. Faint stars in zones or faint companions to bright stars could be measured very rapidly. The relative light of all the asteroids would be an interesting problem. Many coarse clusters appear to consist of stars of nearly equal brightness. Their light compared with their distances apart might aid our study of their formation. Another useful investigation would be to measure the brightness of all the nebulae.

In the application of physics to astronomy doubtless many other problems will suggest themselves. Thus no satisfactory results have

been obtained in the attempt to measure the heat of the stars with the tasimeter. The use of this instrument would be vastly simplified if it was placed on a solid pier near the ground, was not moved during the observation, and could be perfectly protected from other changes of temperature than those which it was intended to measure.

As either of the problems proposed above would occupy the time of a telescope for at least one year, it is obvious that there could be no difficulty in keeping such an instrument occupied indefinitely.

The horizontal mounting is especially adapted to an elevated position, and would permit the use of a telescope where an equatorial mounting would be quite impracticable. On the other hand, to an amateur, or for purposes of instruction, an instrument which could be set quickly from one object to another, and where the observers need not be exposed to the cold, would offer many advantages. The impossibility of observing far from the meridian would be less important with a large instrument, where the number of objects to select from is very great.

There are certain purposes to which this mounting could not be advantageously applied. The study of close double stars and other objects requiring long examination and very perfect definition could be better left to other instruments. The sun, moon, and planets can also generally be better observed off the meridian. If, however, the entire time of an instrument can be employed to advantage, and it can collect several times as much material as an instrument of the usual form, it is no evidence against its trial that there are certain problems to which it cannot be advantageously applied.

The working force required for such an instrument should consist of at least one observer, an assistant to record, and a number of copyists and computers to prepare the working lists, reduce the observations, prepare them for the press, and read and check the proof-sheets. A large volume of valuable observations could thus be produced every year, which would require at least double the time and money to produce by the same telescope mounted equatorially. The difference in the amount of work will be evident when we compare the number of objects observed with a transit instrument per night, with those observed with an equatorial. A hundred objects in various declinations might be examined in a single evening, while it is seldom that the same number could be identified and measured by an equatorial in a week.



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INVESTIGATIONS ON LIGHT AND HEAT, PUBLISHED WITH AN APPROPRIATION FROM THE  
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## XXI.

PHOTOMETRIC MEASUREMENTS OF THE VARIABLE  
STARS  $\beta$  PERSEI AND DM. 81°25, MADE AT THE  
HARVARD COLLEGE OBSERVATORY.

BY EDWARD C. PICKERING, DIRECTOR, ARTHUR SEARLE AND  
O. C. WENDELL, ASSISTANTS.

Presented April 13, 1881.

OUR knowledge of the cause of variation in the light of certain of the fixed stars must be derived largely from the curves showing the intensity of their light at any given time. Two methods may be employed for determining the form of these light-curves, as they are called. First, that proposed by Argelander, in which the variable is compared by the eye with some adjacent stars of nearly equal brightness. The difference, if any, is estimated in terms of a small unit called a grade, which nearly equals a tenth of a magnitude. A discussion of the entire series of measures serves to determine the light of the comparison stars, and to reduce all the measures to a scale of grades. This method is so simple, and gives results of such precision, that it has heretofore been almost exclusively used. For determining the form of the curve qualitatively, and the times of maximum and minimum light, this method leaves little to be desired. For a quantitative study of these curves, however, we must reduce the scale of grades to light ratios by photometric measures of the comparison stars. If, meanwhile, any of the comparison stars vary in light, errors are introduced which cannot be eliminated, and these, with the errors in the photometric measures, are likely to greatly exceed the errors in determining the form of the light-curve. The second method consists in a photometric measurement of the light of the variable at different times, and thus determining directly the form of its light-curve. Although the errors in the final results in the second method may be no larger than in the first, yet they are rendered much more conspicuous, so that hitherto no very satisfactory light-curves have been obtained in this way. On the



other hand, a photometric measure has a great advantage on the score of independence, as it may be repeated many times in succession in a single evening. An observer cannot repeat a naked-eye comparison many times without being prejudiced in the later measures by those which have preceded them.

The photometer used in the following measurements is essentially the same as that described in volume xi. of the *Annals of the Harvard College Observatory*, p. 4, figs. 1 and 2. A double-image prism is placed between the object-glass and eyepiece of a telescope, and in front of the eyepiece a Nicol prism is inserted. A circle divided into degrees serves to show the angle through which the Nicol is turned. Two adjacent stars may be compared by this instrument with great accuracy. Two images of each will be formed by the double-image prism, and their relative brightness varied at will by turning the Nicol. Each image in turn will disappear when the Nicol is revolved  $90^\circ$ . There will therefore always be four positions in which the brighter image of the fainter star will be precisely equal to the fainter image of the brighter star.

#### $\beta$ PERSEI.

The measurements of  $\beta$  *Persei* were made by comparing it with  $\omega$  *Persei*, a fifth magnitude star  $90'$  distant. The two images were formed by two Rochon prisms, which produced a separation of about  $100'$ . It was therefore necessary that they should be placed very near the object-glass of the telescope, in order that the images of the two stars should be near together. The focal length of the telescope is about seventeen inches, and its available aperture is limited by the size of the prisms to about an inch. A larger aperture would be preferable, but is not very important on account of the brightness of the stars. The telescope is placed horizontally with a right-angled reflecting prism in front of the object-glass. The line of sight is therefore horizontal, even when objects in the zenith are observed, and the stars are followed by rotating the telescope around its axis, and also by turning the stand around a vertical axis. The four images are placed in line, and the two central ones, which are compared, are reversed by moving the prisms to and from the object-glass by a handle attached to the tube carrying them. This reversal was essential, and was always made after the second setting in each set. Errors due to the position of the images are thus completely eliminated. As the two images are seen on the same background under precisely the same conditions, many sources of error are eliminated. The conven-

ient position of the observer, the line of sight being always horizontal, also conduces to the accuracy of the measures. Owing to the low power used (about nine diameters), clockwork was not needed, the stars being occasionally brought back to the centre of the field as they moved away. The readings were wholly independent, as it was quite impossible to distinguish the images of the two stars when brought nearly to equality.

The four positions of the Nicol, in which the images appeared to be equal, were read by the graduated circle to tenths of a degree. This was repeated three times, so that twelve settings constituted a single set. Successive sets were commonly taken by different observers, but when one observer only was present he generally took care to leave the instrument for a minute or so between the sets, so that the same sources of error should not recur. Three observers took part in the work, Mr. Arthur Searle, Mr. O. C. Wendell, and myself. They will be designated by the initials S., W., and P.

Observations were made on thirteen nights, from Sept. 29, 1880, to Jan. 1, 1881, and will be detailed in a future volume of the Annals of the Observatory. The total number of sets was 230, containing 2,748 settings, two of the sets being incomplete. Twenty-eight sets were taken when the nearest minimum was five hours or more distant. They serve to determine the full brightness of the variable. Twelve sets by Mr. Searle give the excess in brightness of  $\beta$  over  $\omega$  of 2.45 magnitudes; five by Mr. Wendell give 2.68; and twelve by myself give 2.67. As these results are confirmed by the other observations, we may conclude that  $\omega$  appeared brighter or  $\beta$  fainter to Mr. Searle than to the other observers by about 0.22 magnitudes. All of his measures have been corrected by this amount to reduce all to the same system. Fifty sets, or six hundred readings, were obtained on Oct. 7, extending almost continuously from quarter of seven in the evening to half-past three of the following morning. On Oct. 10, nineteen sets were obtained from half-past six until nearly eleven, when clouds prevented further measures. On Nov. 2, forty-two sets were taken between six o'clock and midnight. On Nov. 19, fifteen sets were obtained; on Nov. 22, thirty-three; on Dec. 9, fourteen; on Dec. 22, nine; and on Jan. 1, twenty-eight. On Nov. 19, the observations of Mr. Searle appeared to differ from the results of the other observers by about three tenths of a magnitude, even after applying the correction of 0.22 magnitudes noted above, or without this correction they differed about half a magnitude. The reduction was first made retaining these, but they introduced so large a discord-

ance that the entire reduction has been repeated, rejecting them. No explanation can be offered for this difference, which occurs in nine sufficiently accordant sets. As the alternate observations of Mr. Wendell on the same evening agreed with the results of the other evenings, the effect seems to be due to the observer, and not to a variation of the star. The remaining observations have been arranged in groups according to the time preceding or following the minimum. Each group extends over half an hour, the computed minimum being the middle of one group. The first and last group extend from 255 to 345, the observations being more scattering. The results derived from these groups are given in Table I. The first column gives the mean of the times before or after the computed minimum. The latter was taken from the *Annuaire* of the Bureau des Longitudes, 1880, p. 78, which depends on the formula given by Schönfeld,\* Ep. E = 1867 Jan. 0<sup>d</sup> 11<sup>h</sup> 1.2<sup>m</sup> M Z Paris + 2<sup>d</sup> 20<sup>h</sup> 48.9<sup>m</sup> (E — 8534).

The second column gives the number of sets in each group, and the third the mean of the observed magnitudes. The points defined by these times and magnitudes were then plotted on rectangular paper, and a smooth curve drawn nearly through them. Various precautions were taken to avoid small irregularities in this curve. The ordinates were read off, and the residuals computed from straight lines nearly tangent to the curve. These were plotted in turn, and the smooth curve drawn through them served to correct the original curve. The discussion of the rate of change in the light and of the true time of minimum, given below, also furnished small corrections, so that the curve should not only pass nearly through the observed points, but should undergo no sudden change in its direction or curvature. The ordinates of the final curve are given in the fourth column, and the deviations of the observations from them in the fifth column.

An inspection of this table shows that the observed minimum precedes that given by computation by more than half an hour. To determine the exact time of minimum, we must find the mean of the times when the light is equal. If the light curve was symmetrical, each of these means would equal the true minimum. Suppose that points are constructed with abscissas equal to the mean times, and ordinates to the corresponding light. Suppose that a smooth curve is drawn through these points, and extended to the point whose ordinate equals the light at the minimum. The abscissa of this point will give

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\* Sechsenddreissigster Jahresbericht des Mannheimer Vereins für Naturkunde, p. 94.

TABLE I.—LIGHT CURVE OF  $\beta$  PERSEI.

Time.	No.	Obs.	Curve.	$O - C.$
—	28	2.67	2.67	.00
— 278	8	2.68	2.67	+ .01
239	10	2.56	2.58	— .02
211	10	2.50	2.48	+ .02
181	9	2.29	2.31	— .02
161	11	2.15	2.14	+ .01
117	9	1.94	1.92	— .02
90	11	1.75	1.76	— .01
59	11	1.68	1.66	+ .02
— 29	11	1.64	1.64	.00
+ 1	17	1.70	1.70	.00
29	12	1.85	1.83	+ .02
63	9	1.98	2.00	— .02
91	12	2.19	2.17	+ .02
122	10	2.29	2.30	— .01
149	11	2.39	2.40	— .01
179	10	2.52	2.50	+ .02
212	10	2.59	2.58	+ .01
239	6	2.60	2.63	— .03
+ 275	6	2.66	2.66	.00
	221			$\pm .013$

the true minimum. Table II. gives for the various magnitudes contained in the first column the corresponding times at which the star attains this brightness during decrease and increase in the second and third column. The mean of these times is given in the fourth column.

TABLE II.—TIME OF MINIMUM.

Magn.	Dec.	Inc.	Mean.
2.6	— 246	+ 221	— 12.5
2.5	— 218	+ 180	— 19.0
2.4	— 196	+ 148	— 24.0
2.3	— 177	+ 122	— 27.5
2.2	— 161	+ 99	— 31.0
2.1	— 145	+ 80	— 32.5
2.0	— 131	+ 63	— 34.0
1.9	— 114	+ 45	— 34.5
1.8	— 97	+ 24	— 36.5
1.7	— 76	+ 1	— 37.5
1.68	— 70	— 5	— 37.5
1.66	— 60	— 13	— 36.5

From the above table we see that the true time of minimum preceded that given in the ephemeris by about thirty-seven minutes. An

ephemeris given by Dr. Schönfeld\* for the present year differs by thirty-five minutes from his formula, or agrees within two minutes with the result of the present observations. The writer has shown in another place† that observations show a deviation from Schönfeld's formula of twenty-nine minutes at the end of 1878, and that this deviation is increasing at the rate of about three minutes a year, which would also give a correction of thirty-five minutes.

Any portion of the observations, as those of a single observer, or of one evening, would in general be better satisfied by moving the curve horizontally, or by assuming a different time of minimum. We wish, therefore, to know what correction  $t$  to the minimum is indicated by such observations. Let  $R$  equal the residual found by subtracting the value given by the assumed curve from that found by observation, and let  $r$  equal the residual when the minimum is altered by  $t$ . Also, let  $a$  equal the differential coefficient of the light in terms of the time, or the change of the light in magnitudes per minute. Then  $R = r + at$ , in which  $r$  and  $t$  are unknown. Solving with regard to  $t$ , we obtain,  $t = \frac{R}{a} - \frac{r}{a}$ . The weight to be assigned to such a determination of  $t$  will be proportional to  $a$ , since the errors are almost entirely due to erroneous determinations of the light, the error in the time being wholly insensible. Accordingly the effect on  $t$  of an error of a hundredth of a magnitude will be inversely as the rate of change of the light, or the weight should be proportional to  $a$ . Whatever the sign of  $a$ , the weight must always be positive. Multiplying the above value of  $t$  by  $a$ , we have  $at = \pm R \pm r$ , in which  $a$  is positive, and the signs of  $R$  and  $r$  will always be those of  $\frac{R}{a}$  and  $-\frac{r}{a}$ . Taking the sum of all these equations, we obtain  $\Sigma at = \Delta R - \Delta r$ , in which  $\Sigma$  denotes the arithmetical sum of all the separate values,  $\Delta$  their algebraic sum, taking into account the signs assigned them above. But  $\Sigma at = t \Sigma a$ , since, although  $t$  is unknown, it is the same for all the observations. Again,  $\Delta r = 0$ , since the separate values of  $r$  are arranged according to accident. Therefore,  $t \Sigma a = \Delta R$ , or  $t = \frac{\Delta R}{\Sigma a}$ . The computation is made by taking the algebraic sum of all values of  $R$  after changing the signs of those, in which  $a$  is negative, and dividing the result by the arithmetical sum of all the values of  $a$ .

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\* Vierteljahrsschrift, xv. 14.

† Proceedings American Academy, xvi. 38.

The probable error,  $e$ , of the resultant value of  $t$  may be found from  $n$ , the number of residuals, their magnitudes  $r$ , and their weights  $a$ . The value of each expressed in minutes will be  $\frac{r}{a}$ , but since a weight of  $a$  should be assigned to it, we must write  $a \times \frac{r}{a} = r$ . The sum of all these terms will be  $\Sigma r$ , and the sum of their weights  $\Sigma a$ . The probable error will therefore be,  $e = \frac{0.845 \Sigma r}{\sqrt{n-1} \Sigma a}$ . We cannot determine  $\Sigma r$  directly, since  $r$  has not been computed. If  $t$  is not very large,  $\Sigma R$  will not greatly exceed  $\Sigma r$ ; we shall not therefore cause a large error if we write  $e = \frac{0.845 \Sigma R}{\sqrt{n-1} \Sigma a}$ . The probable error thus found will be somewhat too large, so that the substitution from which it results cannot exaggerate the accuracy of the observations.  $\frac{\Sigma R}{n}$  equals the average deviation  $D$ , and if  $n$  is large we may write 
$$e = \frac{0.845 \sqrt{n} D}{\Sigma a}.$$

To apply this method we must determine the values of  $R$  and  $a$  corresponding to each set. The light corresponding to the time of each observation was read off from the light curve, and subtracted from the observed brightness. The value of  $a$  was determined as follows: A silk thread was kept stretched perfectly straight by making it the string to a bow of whalebone. It was then laid upon the curve so as to be tangent in turn to the points whose abscissas differ by twenty-five minutes. The ordinates of the points where the thread intersected two vertical lines, whose abscissas differed one hundred minutes, were next read. The difference in these ordinates, divided by one hundred, gave the change in magnitude per minute or  $a$ . Table III. gives, in the first and second columns, the corresponding times and values of  $a$  derived in this way, from the portion of the light curve preceding the minimum. Points were next plotted with the times as abscissas, and the values of  $a$  as ordinates, and a smooth curve drawn through them. The ordinates of this curve are given in the third column, and the residuals found from the observed values of  $a$  in the fourth column. The close agreement testifies to the smoothness of the curve and the precision of the measures. From the curve thus found, the values of  $a$  were read for each set. The last three columns correspond to the portion of the curve following the minimum.

TABLE III.—RATE OF CHANGE IN LIGHT.

Time.	Decreasing.			Increasing.		
	Obs.	Curve.	O — C.	Obs.	Curve.	O — C.
300	—	.0000	—	—	.0000	—
275	—	— .0014	—	—	+ .0007	—
250	— .0030	— .0027	— .0003	—	+ .0013	—
225	— .0037	— .0040	+ .0003	+ .0020	+ .0019	+ .0001
200	— .0054	— .0051	— .0003	+ .0025	+ .0026	— .0001
175	— .0058	— .0059	+ .0001	+ .0031	+ .0031	.0000
150	— .0064	— .0063	— .0001	+ .0035	+ .0038	— .0003
125	— .0063	— .0063	.0000	+ .0041	+ .0045	— .0004
100	— .0056	— .0056	.0000	+ .0048	+ .0050	— .0002
75	— .0036	— .0036	.0000	+ .0059	+ .0054	+ .0005
50	— .0011	— .0013	+ .0002	+ .0054	+ .0054	.0000
25	+ .0008	+ .0010	— .0002	+ .0046	+ .0046	.0000
0	+ .0036	+ .0034	+ .0002	—	—	—

This table also affords a method of determining the point of minimum light. At this point the rate of change should be zero, or should change from positive to negative. This evidently occurs between the times 50 and 25 minutes. Interpolating with the values given in either the second or third column gives for the exact time 36 minutes. This value agrees closely with 37 minutes, the value derived above from the points of equal light. The best method of determining the time of beginning and ending of the variation in light is from this same table. It will necessarily be subject to considerable error, since the observed curve must be extended according to the judgment of the observer. The times — 300 and + 300 have been found in this way. In other words, the star begins to diminish about 263 minutes before the minimum, and does not recover its original brilliancy until 337 minutes after. The most rapid diminution would occur at — 140 or 100 minutes before the minimum. The variation would be then 0.0064 per minute.

The most rapid increase would occur at 100 minutes after the minimum, and would amount to 0.0055 magnitudes per minute.

In Table IV. the values of  $R$  and  $a$  are arranged in groups. A current number in the first column is followed in the second by the condition determining the groups. The next columns give the number of sets of twelve readings each, the arithmetical sum of the values of  $a$ , the arithmetical sum of the residuals, and their algebraic sum, giving to each the sign of  $R$  divided by  $a$ . The seventh column gives the correction to the assumed minimum found by dividing the sixth column by the fourth. The eighth column gives the probable error of the



resulting time, or  $\frac{0.845 \Sigma R}{\sqrt{n-1} \Sigma a}$ . The last column but one gives the average residuals, or the fifth column divided by the third. The last column gives the average deviation of the three sets of four readings each, of which the sets of twelve readings are composed. It serves to show the accordance of the successive readings.

The first seven lines give the results for the seven minima which were observed. The next three lines group together all the observations of each observer. Lines 11 and 12 place together all those in which the light is decreasing, and those in which it is increasing. The results of all these sets is given in line 13. The rejected sets obtained on Nov. 19 are given in line 14. Line 15 groups those in which the star has its full brilliancy, or when the nearest minimum was more than five hours distant. The last line gives the results of lines 13 and 15, or the entire series, excepting those of Nov. 19. A set taken Oct. 7 is also included, which was taken so near the minimum that  $a$  was sensibly equal to zero. For this reason line 16 is not exactly equal to the sum of lines 13 and 15.

TABLE IV.—COMPARISON OF RESULTS.

No.	Group.	No. Sets.	$\Sigma a$	$\Sigma R$	$\Delta R$	$\frac{\Delta R}{\Sigma a}$	Prob. Err.	Av. Resid.	Av. Dev.
1	Oct. 7.....	49	.1937	4.00	—0.62	— 3.2	2.5	.081	.060
2	" 10.....	19	.0837	2.30	+0.28	+ 3.5	5.5	.121	.047
3	Nov. 2.....	43	.1284	2.64	—0.60	— 5.0	2.7	.061	.066
4	" 19.....	6	.0335	0.27	—0.11	— 3.6	3.0	.045	.056
5	" 22.....	33	.1362	3.32	+2.28	+17.5	2.6	.001	.083
6	Dec. 9.....	13	.0353	1.01	+0.11	+ 3.6	7.0	.078	.078
7	Jan. 1.....	28	.1214	2.47	—0.03	— 0.2	3.3	.088	.067
8	Obs. of P.	86	.3103	6.33	—0.35	— 1.2	1.9	.073	.063
9	" S.	45	.1864	5.30	+1.94	+10.4	2.9	.117	.085
10	" W.	60	.2355	4.38	—0.28	— 1.2	2.0	.073	.057
11	Decrease ..	81	.3342	7.27	+0.17	+ 0.5	2.1	.089	.066
12	Increase ..	110	.3960	8.74	+1.14	+ 2.9	1.6	.079	.066
13	Total.....	191	.7322	16.01	+1.31	+ 1.8	1.3	.083	.066
14	Nov. 19. S.	9	.0385	3.55	—3.55	[—92.2]	[27.8]	[.394]	.092
15	Full Light.	28	.0000	3.04	+0.06	—	—	.108	.068
16	Total.....	220	.7322	19.14	+1.28	—	—	.086	.066

The observations of Nov. 22 show a large correction to the minimum. This is not easily explained unless the deviation is real. The measures before the minimum give a correction of +15 minutes; those after, of +18; those of P. alone, +26; of S., +14; of W., +12. As the probable error of the mean result is only 2.6 minutes, and a nearly equal number of measures were made on each side of

the minimum, it is difficult to understand what instrumental errors could have caused the deviation. Including this minimum, the mean deviation for the seven nights is 5.2 minutes, or excluding the observations of Nov. 22, 3.2 minutes, the corresponding probable error would equal 4.7 and 3.0 minutes. The mean of the probable errors given in the next column is 3.8 minutes. This compares favorably with the results of naked-eye observations. Schmidt\* gives the probable error of a single minimum observed by Argelander to be 6.0 minutes; of those of Schönfeld, 4.6 minutes; and of those by himself, 8.0 minutes. Probably still better results could have been obtained photometrically had the observations been designed for determining the time of minima. The mean of the whole series of measures would imply a correction to the adopted curve of  $+1.8$  minutes, with a probable error of 1.3 minutes. But if the observations of Nov. 22 are rejected, the correction becomes  $-1.6$  minutes. It therefore seems better to retain the correction to the ephemeris of 37 minutes, already adopted.

We have now a means of determining more precisely the constant difference between the different observers. The differences so far assumed are,  $P = 0.00$ ,  $S = -0.22$ , and  $W = 0.00$  magnitudes. If either observer had taken an equal number of observations before and after the minimum, — or more strictly, if the weight of his observations before and after the minimum were equal, — an error in this correction would not affect the result. It would, however, very slightly exaggerate the residuals, and consequently the probable errors. If these personal differences were zero, the algebraic sum of the residuals of each observer should be zero. In fact, their values for the three observers are, for  $P = -2.43$ , for  $S = +1.66$ , and for  $W = +1.84$ . As the total number of sets in the three cases are 98, 57, and 64, we obtain by division the deviations  $-0.02$ ,  $+0.03$ , and  $+0.03$ . Combining with these the correction of 0.22 already derived from Mr. Searle's observations of the full light of the variable, we find that the correction required to reduce his measures to mine is  $+0.17$ , and to reduce Mr. Wendell's  $-0.05$  magnitudes. The effect of these changes on the final result would probably be wholly insensible.

Line 14 of the above table shows clearly that the observations of Nov. 19 should be rejected. They would indicate an error of an hour and a half in the minimum, if the deviations were not so large that the present method could not be applied.

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\* Astron. Nach., lxxxvii. 204.

A comparison may now be made with the light-curve given by Schönfeld in the paper cited above. As has been already stated, the great difficulty lies in deciding what brightness shall be assumed for the comparison stars. In a previous article,\* the light of these stars in grades assumed by Schönfeld have been reduced by means of the formula  $L = 8.446 + 0.025 g$ , in which  $L$  gives the light and  $g$  the number of grades. This formula is derived from a comparison with the measurement of the comparison stars by Seidel and Wolff. These stars have since been measured with the meridian photometer of the Harvard College Observatory. Each star has been observed on the average on ten nights.

Three methods of reducing the grades of Schönfeld by these stars may be used. We may adopt the formula given above, which was found by a least square solution of the measures of Seidel and Wolff. Secondly, we may apply the method of least squares to the Harvard College Observatory measures, and deduce the formula most nearly satisfying them. This gives the value of one grade in logarithms equal to 0.029. In both these cases we have assumed that the value of a grade is the same for bright and for faint stars, and that the deviations are due to accidental errors, or to variations which have taken place in the light of the stars. As a third method, we may draw a curve through the points whose co-ordinates equal the light in grades and the measured brightness, and reduce the grades by means of this curve. We now assume that the errors are unimportant, but that the grade varies in different parts of the scale.

Table V. gives, in successive columns, the name of the star, its light in grades, the number of nights on which it has been observed at Cambridge, the resulting magnitude, the probable error, and the logarithm of the light, adopting the same unit as that of Seidel. Observations of  $\beta$  *Persei* have been included in this list, excluding those made within a few hours of its minimum. Three columns of residuals exhibit differences between the measures of Seidel, of Wolff, and of the Harvard College Observatory, and the values computed by the formula  $L = 8.446 + 0.025 g$ . The next column gives the H. C. measures reduced to logarithms, minus those given by the formula  $8.391 + 0.029 g$ . The last column gives the difference between the measures of the stars and the values of their light derived from the smooth curve.

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\* Proc. Am. Acad., xvi. 21.

The last two lines give the mean results in logarithms and in magnitudes.

TABLE V.—COMPARISON STARS OF  $\beta$  PERSEI.

Name.	Gr.	No. Nights	Mag.	P. E.	Log.	S-C.	W-C.	HC-C	HC-C'	HC- Curve.
$\gamma$ Andromedæ.	23.4	11	1.89	.05	9.085	+.007	-.010	+.054	+.015	.000
$\beta$ Persei.....	20.8	13	2.05	.03	9.021	—	—	+.045	+.017	.000
$\epsilon$ Aurigæ.....	17.3	3	2.40	.12	8.881	-.181	-.075	+.003	-.011	.000
$\beta$ Arietis.....	16.7	12	2.48	.05	8.849	+.033	-.002	-.015	-.027	-.006
$\epsilon$ Persei.....	12.8	10	2.75	.06	8.741	+.034	-.020	-.025	-.021	-.002
$\gamma$ Persei.....	10.9	10	2.85	.03	8.701	-.019	-.027	-.017	-.006	-.007
$\beta$ Trianguli...	9.1	14	2.86	.04	8.697	+.042	+.042	+.023	+.042	+.003
$\delta$ Persei.....	7.8	11	2.90	.05	8.681	+.100	+.053	+.040	+.064	+.011
$\alpha$ Trianguli...	3.5	12	3.26	.05	8.537	-.003	+.054	+.003	-.016	-.001
$\nu$ Persei.....	0.9	10	3.71	.06	8.357	—	-.033	-.111	-.060	.000
Mean in logarithms .....				±.020		±.052	±.045	±.034	±.028	±.003
Mean in magnitudes .....				±.05		±.13	±.11	±.08	±.07	±.01

The eighth and ninth columns show that the agreement of our measures with the estimates of Schönfeld is better than that of either Seidel or Wolff. This is the case even when the value of  $g$  is derived from the measures of these observers. The last column shows that a curve could be made to follow the observations almost exactly, the small deviations being allowed rather than that too sharp a change of curvature should be given to the curve.

The form of light-curve deduced from the above measures is shown in Table VI. The first column gives the time, and the second the corresponding magnitude, found by reading the ordinates of the curve drawn through the observed points as described above. A correction to the ephemeris of thirty-seven minutes in the time of minimum is assumed, and the points correspond to intervals of thirty minutes from this time. The logarithm of the light is given in the third column, and is found by multiplying the magnitudes by 0.4 and subtracting 1.068. The relative intensity of the light compared with the full brightness is given in the next column. The observations of Schönfeld are next reduced by assuming the value of  $g$  to be successively 0.025 and 0.029; and, thirdly, by means of the curve described on page 380. The residuals in the last three columns are found by subtracting the logarithms given in the third column from these three sets of values.

TABLE VI.—LIGHT CURVE OF  $\beta$  PERSEI.

Time.	Mag.	Log.	Light.	Schönfeld.		
				$g = .025$	$g = .029$	Curve.
— 4 30	2.67	0.000	1.000	—	—	—
4 0	2.67	0.000	1.000	— .014	— .016	— .023
3 30	2.60	.972	.938	— .002	— .007	— .018
3 0	2.50	.932	.855	+ .015	+ .007	— .013
2 30	2.35	.872	.745	+ .042	+ .028	— .012
2 0	2.18	.804	.637	+ .058	+ .036	— .018
1 30	1.98	.724	.530	+ .057	+ .022	— .014
1 0	1.80	.652	.449	+ .040	— .009	+ .008
— 0 30	1.68	.604	.402	+ .032	— .025	+ .010
0 0	1.64	.588	.387	+ .031	— .030	+ .005
+ 0 30	1.68	.604	.402	+ .031	— .027	+ .008
1 0	1.79	.648	.445	+ .022	— .031	— .004
1 30	1.94	.708	.510	+ .017	— .027	— .025
2 0	2.12	.780	.603	+ .029	— .002	— .051
2 30	2.26	.836	.686	+ .038	+ .019	— .037
3 0	2.39	.888	.773	+ .035	+ .023	— .012
3 30	2.48	.924	.840	+ .036	+ .030	+ .012
4 0	2.56	.956	.904	+ .030	+ .028	+ .022
4 30	2.63	.984	.964	+ .016	+ .0 6	+ .016
5 0	2.66	.996	.991	+ .004	+ .004	+ .004
+ 5 30	2.67	0.000	1.000	—	—	—
Mean in logarithms .....				$\pm .029$	$\pm .019$	$\pm .016$
Mean in magnitudes .....				$\pm .07$	$\pm .05$	$\pm .04$

It does not seem to be practicable to obtain at present more accurate values from the observations of Dr. Schönfeld, on account of the uncertainty in the value of a grade. The observations themselves are much more precise, and determine the time of minimum, as has been shown above, with an accuracy nearly equal to that of the photometric measures. Even if more accurate measures of the comparison stars should be made, we should still be in doubt whether to assume that  $g$  is constant, or that the reduction should be made, as in the last column, by a curve. From the residuals it appears that the various deduced values differ from each other more than they differ from the photometric measures. It accordingly appears scarcely safe to correct the latter by the former. The three values of the minimum corresponding to the last three columns are 1.72, 1.56, and 1.65 magnitudes, their mean agreeing exactly with the photometric measure of 1.64.

It is to be noticed that the value of  $g = 0.029$  is confirmed by the photometric measure of  $\beta$  Persei, since the residuals are less than when  $g$  is taken equal to 0.025. A wholly independent test of the accuracy of the meridian photometer measures is thus afforded. Since

the residuals are smallest in the last column, it seems probable that the value of a grade is not always the same.

The results of the two methods agree as closely as would be expected, even if no systematic errors increased their discordance. The residuals of the photometric observations indicate a probable error of 0.024 magnitudes for each group. Assuming an equal accordance in the observations of Schönfeld, the two methods should differ by 0.04, or by the amount found in Table VI.

#### DM. 81°25.

The variability of this star was detected by M. Ceraski, of Moscow, during the summer of 1880. It was soon shown that it belonged to the Algol class, or that every few days it lost a large portion of its light for several hours; the interval in the case of this star is somewhat less than two days and a half. Measurements of its light were made according to the method described above in the case of  $\beta$  *Persei*. The photometer was attached to the 15-inch telescope of the Harvard College Observatory, since as much light-gathering power as possible was desired, owing to the faintness of the star. The same observers took part in the work, and the observations were made in the same way as with  $\beta$  *Persei*, except that the images were reversed by turning the photometer instead of by moving the prism. This could be done very conveniently by a pinion, which served to rotate the entire tail-piece of the telescope. The prism was therefore set once for all, and the images reversed and separated by any desired amount with great nicety by turning a milled head. The star DM. 81°26, which is estimated in the *Durchmusterung* to be of the 9.5 magnitude, and is nearly north at a distance of 5', was used for comparison. DM. 81°30 would have been better on account of its greater brightness, but its distance of 8' is so great that both images could not be easily brought together. The large angle of the prisms and their distance from the object-glass rendered the light-pencils divergent. At first this gave much trouble, but it was remedied by placing the images always in the same part of the field. Two cardboard points visible against the background of the sky secured this condition. The great northern declination reduced the errors of the driving clock to about one sixth of what they would be for an equatorial star.

The first measures to determine the full brightness of the variable in terms of that of the comparison star were made on February 6, 1881. On the following evening the variable attained its minimum at about half-past eleven. Forty sets or four hundred and eighty settings were obtained between a quarter past six and half past ten. The

later observations were made through clouds which finally stopped the measurements. On February 17 seventy-five sets or nine hundred settings were obtained; the observations extended from seven o'clock in the evening until the variable had regained its full light, at about half-past two on the following morning. During this time no interval of more than five minutes elapsed during which an observer was not comparing the two images. During most of the time the observers took sets alternately, so that there was only an interval of a few seconds between the sets. On February 22 observations began at half past six and continued until ten o'clock, when they were stopped by clouds. Twenty-six sets were obtained in this time. A long period of cloudy weather intervened, and the next measures were made on March 24. Thirty-six sets were taken through clouds, from quarter-past nine to quarter-past twelve. Owing to the small distance between the stars, no perceptible error seems to be introduced by these clouds, as long as they are not dense enough to render the stars invisible. Some measures were obtained on March 14, but apparently the wrong star was observed. They were stopped by the deposition of dew on the object-glass, which may have caused an error, since the two pencils include different portions of the objective. No use has been made of these observations. On April 3 another minimum was observed. Fifty-two sets of six hundred and twenty-four settings were made between seven o'clock and midnight, when the star had recovered its full brightness. Forty-four sets of five hundred and twenty-eight settings were also made on other evenings to determine the undiminished light of the star. Fifteen of these sets by Mr. Searle give its light as 3.64 magnitudes brighter than DM. 81°26. Sixteen sets by Mr. Wendell gave 3.59, and thirteen sets by myself gave 3.71. As the evidence of systematic difference is not conclusive, the mean of all, or 3.64, has been adopted.

The entire number of measures, not including those of March 14, is 273 sets or 3276 settings.

Table VII., like Table I., gives the results of these measures arranged in groups in the order of times from the computed minimum. The columns give the mean of the times, the number of sets of twelve settings, the mean magnitude, the corresponding magnitude derived from a curve drawn nearly through them, and the difference of the last two columns. Each group extends over thirty minutes, except the first, which extends from -311 to -258, and the last three, which include all the measures made when the nearest minimum was more than five hours distant. Their limits are +852 to +991, +1350 to +1495, and +1887 to +2250 minutes.



TABLE VII.—LIGHT-CURVE OF DM. 81°25.

Time.	No.	Obs.	Curve.	O — C.
— 286	6	3.39	3.45	— .06
237	8	3.30	3.27	+ .03
208	14	3.07	3.09	— .02
178	11	2.91	2.85	+ .06
148	15	2.44	2.44	.00
118	14	1.81	1.80	+ .01
89	14	1.34	1.33	+ .01
62	14	1.27	1.25	+ .02
31	12	1.16	1.24	— .08
— 3	9	1.29	1.24	+ .05
+ 31	12	1.28	1.24	+ .04
60	14	1.32	1.32	.00
90	18	1.93	1.93	.00
120	17	2.48	2.48	.00
150	14	2.94	2.93	+ .01
179	14	3.22	3.23	— .01
207	15	3.42	3.42	.00
237	8	3.54	3.54	.00
922	12	3.66	3.64	+ .02
1411	19	3.65	3.64	+ .01
+2127	13	3.62	3.64	— .02
	273			±.019

From the last three groups we may infer that the light of this star, like that of the others of the same class, is constant except during the few hours immediately preceding or following the minimum.

The same precautions were taken as with  $\beta$  Persei in drawing the light-curve that it should be free from sudden changes in curvature. From the small residuals in the last column we may therefore infer that the accidental errors are very small. About an hour before the minimum the light ceases to vary, and remains nearly constant for an hour and a half, when it begins to rapidly increase. The exact time of these changes may be found more precisely by subdividing the groups whose means are —89 and +60. Making the period of the groups ten minutes instead of thirty, we replace the first group by three containing 4, 5, and 5 sets, having mean times 99, 90, and 80, and magnitudes 1.54, 1.30, and 1.21. The other group similarly subdivided gives for the mean times 52, 60, and 69, the magnitudes, 1.25, 1.26, and 1.44. From these we might infer a somewhat longer period of uniform light than would be indicated by the curve already drawn. The number of observations is, however, too small to determine this point with certainty.

The correction to the ephemeris of the minima is best found by Table VIII., which gives the time at which the light is equal while

decreasing and while increasing. The successive columns give the light in magnitudes, the corresponding times before and after the minimum, and the mean of these times.

TABLE VIII.—TIME OF MINIMUM.

Magn.	Dec.	Inc.	Mean.
3.6	—362	+256	—53.0
3.5	—305	+225	—40.0
3.4	—270	+204	—33.0
3.3	—246	+190	—28.0
3.2	—226	+175	—25.5
3.1	—209	+164	—22.5
3.0	—194	+155	—19.5
2.9	—182	+147	—17.5
2.8	—173	+140	—16.5
2.7	—164	+133	—15.5
2.6	—157	+127	—15.0
2.5	—151	+121	—15.0
2.4	—146	+115	—15.5
2.3	—141	+109	—16.0
2.2	—137	+104	—16.5
2.1	—132	+99	—16.5
2.0	—128	+94	—17.0
1.9	—123	+88	—17.5
1.8	—117	+83	—17.0
1.7	—112	+78	—17.0
1.6	—107	+73	—17.0
1.5	—101	+68	—16.5
1.4	—94	+64	—15.0
1.3	—87	+59	—14.0

From the numbers in the last columns we may infer a correction of 13 minutes when the light equals 1.24, or at the minimum. In other words, thirteen minutes should be subtracted from the adopted ephemeris of the minima. The minimum can evidently be determined with much precision from any observations of the times at which the light is equal when diminishing and increasing. If the light is less than 2.9, or the interval between the times less than five hours and a half, it is only necessary to take the mean of the two times and subtract from two to four minutes. The exact correction is found from the last column of the table after subtracting thirteen minutes. The observation is easily made with a small telescope, as there are so many comparison stars of suitable brightness near the variable. Doubtless a very precise determination of the minimum could thus be easily obtained.

To reduce the separate observations we must determine the rate of change in light. The method employed for  $\beta$  *Persei* has again been used; the results are given in Table IX. The columns have the same meaning as in Table III.

TABLE IX.—RATE OF CHANGE IN LIGHT.

Time.	Decreasing.			Increasing.		
	Obs.	Curve.	O — C.	Obs.	Curve.	O — C.
300	—	— .0003	—	—	+ .0004	—
275	—	— .0017	—	—	+ .0012	—
250	— .0040	— .0032	— .0008	+ .0026	+ .0024	+ .0002
225	— .0057	— .0050	— .0007	+ .0040	+ .0040	.0000
200	— .0067	— .0073	+ .0006	+ .0063	+ .0054	+ .0009
175	— .0106	— .0108	+ .0002	+ .0086	+ .0088	— .0002
150	— .0180	— .0171	— .0009	+ .0125	+ .0125	.0000
125	— .0198	— .0201	+ .0003	+ .0166	+ .0162	+ .0004
100	— .0157	— .0152	+ .0005	+ .0188	+ .0196	— .0008
75	— .0025	— .0024	— .0001	+ .0205	+ .0198	+ .0007
50	.0000	— .0006	+ .0006	+ .0026	+ .0030	— .0004
25	.0000	.0000	.0000	.0000	.0000	.0000
0	.0000	.0000	.0000	.0000	.0000	.0000

The greatest change in light amounts to two hundredths of a magnitude a minute, or at the rate of a magnitude and two tenths an hour. This is much greater than the change of any other known variable, being over three times that of  $\beta$  Persei. Accordingly, we should expect a corresponding increase in the accuracy with which the time of minima could be determined.

The observations of DM. 81°25 are grouped in Table X. The successive columns, like those of Table IV., give a current number, the condition limiting the group, the number of sets, the arithmetical sum of the residuals, their algebraic sum giving to each the sign of  $R$  divided by  $a$ , and the correction to be inferred, or  $\Delta R$  divided by  $\Sigma a$ . The remaining columns give the probable error, the average of the residuals, and the average difference of the three sets of four contained in each set of twelve settings.

TABLE X.—COMPARISON OF RESULTS.

No	Group.	No. Sets.	$\Sigma a$	$\Sigma R$	$\Delta R$	$\frac{\Delta R}{\Sigma a}$	Prob. Err.	Av. Dev.	Av. Resid.
1	Feb. 7....	38	.3463	8.31	— .35	—1.0	1.3	.087	.065
2	" 17....	62	.7071	7.55	+ .01	0.0	1.1	.121	.063
3	" 22....	23	.2408	2.49	— .01	0.0	1.9	.108	.082
4	March 24..	36	.4312	3.03	+ .35	+0.8	1.0	.084	.059
5	April 3....	38	.4000	3.22	+ .74	+1.8	1.1	.084	.051
6	Obs. of P..	76	.8618	6.41	— .01	0.0	0.7	.084	.055
7	" S..	69	.7248	9.11	+1.69	+2.3	1.3	.132	.072
8	" W..	52	.5388	4.08	— .94	—1.7	0.8	.078	.062
9	Decrease ..	91	.9089	9.23	+ .39	+0.4	0.9	.101	.071
10	Increase ..	106	1.2165	10.37	+ .85	+0.3	0.6	.097	.055
11	Total.....	197	2.1254	19.60	+ .74	+0.3	0.6	.099	.062

The average probable error of the five minima observed is 1.3 minutes, or about one third of that of  $\beta$  *Persei*. This ratio, as has been already stated, was to be expected, since the rate of variation of the stars is about as three to one. The average deviations from the ephemeris, after applying the constant correction of thirteen minutes, is only 0.7 minutes. It becomes still less if we adopt another ephemeris, as will be shown below. Clouds or twilight prevented observations on both sides of the minimum on every night except on February 17. Accordingly, from a complete observation of a minimum under favorable circumstances we may expect an error of but a few tenths of a minute.

The systematic difference between the observers is found by dividing the algebraic sum of the residuals of each by their number: the algebraic sum of 86 residuals by Mr. Searle is  $-5.30$ ; of 85 by Mr. Wendell,  $-0.87$ ; and of 102 by myself,  $+5.62$ . The corresponding corrections are,  $-0.06$ ,  $-0.01$ , and  $+0.06$ . As each of these represent over a thousand settings, the differences are not probably due to accident. The excess of the computed probable error in the eighth column of Table X. over that to be inferred from the residuals in the seventh column is partly due to the neglect of these differences. If applied to the observations, they would make them appear more accordant. They would not probably sensibly affect the form of light-curve or the times of minima, owing to the distribution of the measures of each observer.

The variation in light is given in Table XI., which is derived from the light-curve described above, after applying a correction of thirteen minutes to the assumed minimum. The ratios of light are given for every half-hour, expressed in differences of magnitude, in logarithms, and in numbers, the full brightness being assumed as the unit in the last two columns.

Some interesting theoretical deductions may be drawn from this light-curve. For about an hour and a half the light remains sensibly constant at 0.110, or about one ninth of its full intensity. This interval is over one third of that during which the light is increasing or diminishing. If the variation in light is admitted to be due to a dark, eclipsing satellite, the diameter of the latter must be  $\sqrt{1 - 0.110} = 0.943$  of that of the star, in order to sufficiently reduce the light. A somewhat less diameter is possible if we admit that the star, like our sun, is darker near the edges than in the centre. The effect of this is probably slight, or it would show itself in other ways. The longest period of uniform minimum light would occur if the satellite produced a central

TABLE XI.—LIGHT-CURVE OF DM. 81°25.

Time.	Mag.	Log.	Light.
h. m.			
-6 30	3.64	0.000	1.000
6 00	3.62	9.992	0.982
5 30	3.58	9.976	0.946
5 00	3.52	9.952	0.895
4 30	3.44	9.920	0.832
4 00	3.34	9.880	0.759
3 30	3.19	9.820	0.661
3 00	2.99	9.740	0.550
2 30	2.68	9.616	0.413
2 00	2.12	9.392	0.247
1 30	1.71	9.228	0.169
1 00	1.27	9.052	0.113
-0 30	1.24	9.040	0.110
0 00	1.24	9.040	0.110
+0 30	1.24	9.040	0.110
1 00	1.26	9.048	0.112
1 30	1.67	9.212	0.163
2 00	2.26	9.448	0.281
2 30	2.76	9.648	0.445
3 00	3.13	9.796	0.625
3 30	3.35	9.884	0.766
4 00	3.51	9.948	0.887
4 30	3.59	9.980	0.955
+5 00	3.64	0.000	1.000

annular eclipse. In this case, if the motion was uniform, the duration of the minimum light would equal only one ninth of that of increase or decrease. The effect of the curvature, or ellipticity, of the path would not greatly affect this conclusion. A very great ellipticity is not admissible, or at the periastron the satellite would strike the star. We are therefore obliged to admit that the eclipse is total (that is, that the star is entirely covered by the satellite), and that the light during the minima is due to one of the two following causes: first, that the satellite is self-luminous, and that the light at the time of the minimum is that received from the satellite, the star itself being completely obscured. In this case we should expect to find a corresponding diminution midway between the minima when the star was in front of the satellite, and accordingly cut off a portion of its light. The loss of light would, however, be small, and might easily escape detection. The greatest effect would occur when the transit was central. In this case, to produce the observed duration of the minimum, assuming the motion to be uniform, the diameter of the satellite should be about 1.3, that of the star being taken as unity. Since the light of the satellite is supposed to be 0.110, that of the satellite and star together being taken as unity, it follows that if the star passes in front of the satel-

lite, it will cut off  $\frac{1}{(1.3)^2}$  of its light, or produce a diminution in the total light of  $\frac{1}{(1.3)^2} \times 0.110 = 0.065$ . The secondary minimum would therefore reduce the light from 1.000 to  $1.000 - 0.065 = 0.935$ , or about 0.07 magnitudes. This will be the greatest effect, and would be less if the transit was not central. An eccentricity in the orbit of the satellite might even reduce it to zero by carrying the satellite at superior conjunction entirely to one side of the star.

The light reflected by the satellite from the star does not account for this phenomenon, since during its transit the dark side of the satellite would be turned toward the observer. In no case would the light reflected be sufficient, because the satellite does not receive one ninth of the light of the primary; so that, even if all were reflected, it could not emit a sufficient amount of light.

A second hypothesis would explain the prolonged diminution of light by admitting that the satellite consisted of a cloud of meteors so scattered that about 0.110 of the light could pass through the central portions. We should then expect that somewhat more light would pass through the edges, and accordingly that the light would vary slightly during the whole obscuration, attaining a true minimum when the centres of the star and satellite appeared to coincide.

In a recent note Dr. Vogel informs me that he has found no perceptible approach or recession of Algol by means of the spectroscope.\* If this observation is confirmed with the other similar variables, we should infer that the masses of the eclipsing satellites were small, or that the second hypothesis is the more probable of the two. In any case, an excellent example is afforded of the value of indirect observations, like those with the photometer or spectroscope, in solving certain problems where direct measurements are valueless.

The next step is to compare the results of other observers, and to derive the correction to the ephemeris. Following the example of Argelander by reducing to Paris mean time, the ephemeris for the time at which any minimum will occur may be expressed by the formula, —

$$\text{Time of minima} = 1880 \text{ June } 23^{\text{d}} 7^{\text{h}} 44.0^{\text{m}} + 2^{\text{d}} 11^{\text{h}} 50.0^{\text{m}} E.$$

The number of minima which have elapsed since the discovery of the variability is here designated by  $E$ , which accordingly equals zero

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\* See also Ber. der Königl. Säch. Gesell. xxv. 555, and Proc. Amer. Acad. xvi. 34.

on June 23, 1880. The first observations which can be reduced are those made by M. Glasenapp\* on July 3, 1880. He adopted a series of comparison stars, which will probably be employed by other observers of this variable. Table XII. gives their Durchmusterung designations, and their right ascension, declination, and magnitudes taken from that catalogue. The next columns give the designation by Glasenapp, and the assumed light in grades. Measures of these stars were made on three evenings at the Harvard College Observatory with Photometer I.† attached to a telescope of four inches aperture. These measures must be regarded as provisional; a much more precise determination of their light will probably be obtained next year with a large meridian photometer. From these measures, which are given in the seventh column, the grades of M. Glasenapp are reduced to magnitudes by the formula,  $m = 9.5 - 0.07 g$ , in which  $g$  denotes the number of grades and  $m$  the corresponding magnitude. The results are given in the eighth column. The last two columns give the residuals found by subtracting the H. C. measures from the magnitudes of M. Glasenapp and of the Durchmusterung.

TABLE XII.—COMPARISON STARS FOR DM. 81°25.

DM.	R.A.		Dec.	Mag.	Desig.	Gr.	H.C.	G.	G-HC.	DM-HC.
	m.	s.	°							
80°23	41	14	80	57.8	9.2	c	0.0	9.6	9.5	-0.1
81°22	42	04	81	07.5	9.2	d	1.6	9.4	9.4	0.0
80°22	40	28	80	53.3	9.2	b	2.0	9.2	9.4	+0.2
80°21	39	05	80	48.9	8.9	a	4.6	8.9	9.2	+0.3
81°27	50	56	81	19.3	8.6	(3)	12.1	8.5	8.6	+0.1
81°29	51	35	81	28.1	8.6	(4)	12.6	8.8	8.6	-0.2
81°18	38	28	81	10.5	7.6	(5)	17.6	7.5	[8.3]	[+0.8]
81°30	52	29	81	10.9	8.3	(2)	18.3	8.1	8.2	+0.1
81°25	49	39	81	05.6	7.5	—	—	6.9	—	—

The star DM. 81°18 is either variable, or its light in grades is erroneously given by M. Glasenapp. An examination on different evenings showed that it was decidedly brighter than 81°30. This is confirmed by the measures and by the Durchmusterung magnitudes. If the light in grades was written 17.6 by mistake for 27.6, the magnitude becomes 7.6 instead of 8.3, and the residual + 0.1 instead of + 0.8. This cannot be a typographical error, since the stars were arranged by M. Glasenapp in the order of brightness, and 81°18 is

\* Astron. Nach., xviii. 61.

† Annals, xi. p. 7, figs. 5 and 6.



placed before 81°30. The other residuals show a good agreement between the estimates and measures. The Durchmusterung magnitudes also agree well, if we correct for the difference of scale, which makes the residuals for faint stars negative and for bright stars positive.

The individual comparisons by M. Glasenapp are detailed in Table XIII., which gives a current number, the Moscow mean time, and the corresponding light in grades. By the formula  $1.00 + 0.07g$  these are reduced to the same scale of magnitudes as that used in measuring the light in Table XI. The results are given in the fourth column. The next column gives the time of minimum derived from each of these observations by means of the light-curve adopted in Table XI. The last column gives the error in the observation of M. Glasenapp, if we assume the minimum to have occurred at 9<sup>h</sup> 47<sup>m</sup> Moscow mean time.

TABLE XIII.—M. GLASENAPP'S COMPARISONS OF DM. 81°25 ON JULY 8

No.	M.M. T.	Gr.	Log.	Time Min.	O — C.
1	10 40	4.1	1.28	<sup>h.</sup> <sup>m.</sup> [ 9 34]	+.03
2	43	2.2	1.15	—	— .10
3	45	4.8	1.34	[ 9 31]	+.08
4	50	3.4	1.24	—	— .02
5	55	3.6	1.25	[ 9 59]	— .03
6	57	4.8	1.34	[ 9 43]	+.05
7	11 1	5.4	1.38	9 45	+.04
8	8	6.8	1.48	9 47	.00
9	12	8.1	1.57	9 47	.00
10	15	8.8	1.62	9 48	— .01
11	17	9.3	1.65	9 48	— .02
12	19	12.3	1.86	9 40	+.15
13	22	10.4	1.73	9 47	— .05
14	24	13.5	1.94	9 40	+.13
15	27	11.8	1.83	9 49	— .05
16	31	12.2	1.85	9 52	— .10
17	37	13.2	1.92	9 54	— .14
18	41	14.2	1.99	9 55	— .15
19	51	14.5	2.02	[10 04]	[— .30]
20	59	14.5	2.02	[10 12]	[— .44]
21	12 23	16.2	2.13	[10 29]	[— .72]
22	47	17.2	2.20	[10 50]	[— .93]
23	13 23	17.4	2.32	[11 19]	[— 1.08]

The error in the estimated light of DM. 81°18 seems to have affected the last measures of the variable. It would appear that after increasing for over two hours (or three hours after the minimum), the variable had not attained the brightness of DM. 81°30, or 18.3 grades! The last five observations have accordingly been bracketed. The

second and fourth comparisons cannot be reduced, since the light is less than that adopted for the minimum. All of those preceding eleven hours have also been bracketed, since the variation in light is so small that an exceedingly small weight should be assigned to them. Retaining them would not sensibly affect the result. The mean of the remaining twelve gives for the time of minimum  $9^h 47^m$  Moscow mean time. The proximity of the minimum does not affect the residuals of the last column. The last five are alone rejected, since, owing to the cause stated above, they indicate errors too large to be accidental. The mean of the eighteen residuals retained is 0.06 magnitudes.

The most complete series of naked-eye observations of this variable are those of Dr. Schmidt of Athens. Five minima were observed by him in August.\* As all the comparisons were made after the period of least light, he was obliged to wait for their reduction until October 8, when he observed the star both before and after the minimum. The first reduction of these observations was made from a curve derived from the measures of October 8. Later he has given a discussion of thirteen minima,† from which he infers a rapid increase in the period. In this paper he omits the observations of August 22, although in his former paper he had assigned to it and to the minimum of August 17 weights double those of any of the others. No reason is given for this omission. There also seems to be a misprint in line 12, p. 89, of this same article. December 7 should apparently be December 2, as this date is employed below. Otherwise, an error of nineteen minutes would be indicated in the observed minimum. A second reduction is given of the August observations, by which the time of minimum is increased more than half an hour. As the original comparisons have not been published, it is impossible to rediscuss them. As the star varies only a few hundredths of a magnitude during nearly two hours, it is obvious that large differences may arise in the assumed time when the light is least. Dr. Schmidt has also determined the period by a method free from this criticism. He has compared the intervals between the times at which the variable equals one of the comparison stars in brightness. Unfortunately, he has not stated the times at which this occurs, so that a comparison with other observers is not practicable.

Mr. George Knott has also observed seven of the minima by the method of Argelander.‡ On September 23 and 28 the variable was

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\* Astron. Nach., xcvi. 283.

† Astron. Nach., xcix. 87.

‡ Astron. Nach., xcix. 109. Nature, xxiii. 542.

observed at the Harvard College Observatory by the same instrument which was used in determining the light of the comparison stars. The image of *α Ursae Minoris* was rendered equal to the variable and to DM. 81°30 alternately. Seven settings were made in each set, beginning and ending with the variable. Systematic errors were thus greatly reduced, since those only would enter which affected one star and not the other. Although a large number of readings were taken, the results were not satisfactory and probably have but little value. The result for September 23 was 8<sup>h</sup> 57<sup>m</sup>, Cambridge mean time, and for September 28, 8<sup>h</sup> 7<sup>m</sup>, the difference between the two being five days less fifty minutes instead of five days less twenty minutes. On neither evening were observations obtained before the minimum, owing to twilight.

TABLE XIV.—COMPARISON OF OBSERVED MINIMA.

No.	E.	Comp. Time.			Obs.		Meridian.	O — C.	Authority.
		d.	h.	m.	h.	m.			
1	0	June	23	7 44	—	—	—	—	Ceraski.
2	4	July	3	7 04	9	47	Moscow.	+22	Glaserapp.
3	16	Aug.	2	5 04	7	10	Athens.	+40	Schmidt I.
4	"	"	"	"	7	53	"	+83	Schmidt II.
5	18	Aug.	7	4 44	6	54	"	+44	Schmidt I.
6	"	"	"	"	7	30	"	+80	Schmidt II.
7	20	Aug.	12	4 24	6	15	"	+25	Schmidt I.
8	"	"	"	"	7	03	"	+73	Schmidt II.
9	22	Aug.	17	4 04	5	41	"	+11	Schmidt I.
10	"	"	"	"	6	28	"	+58	Schmidt II.
11	24	Aug.	22	3 44	5	21	"	+11	Schmidt I.
12	37	Sept.	23	13 34	8	57	Cambridge.	+17	H. C. O.
13	30	"	28	13 14	8	07	"	+13	"
14	43	Oct.	8	12 34	14	16.5	Athens.	+16.9	Schmidt.
15	47	"	18	11 54	13	33.6	"	+14	"
16	49	"	23	11 34	11	27	Greenwich.	+02	Knott.
17	51	"	28	11 14	12	44.0	Athens.	+4.4	Schmidt.
18	53	Nov.	2	10 54	12	31.0	"	+11.4	"
19	"	"	"	"	11	0	Greenwich.	+15	Knott.
20	55	Nov.	7	10 34	11	55.3	Athens.	+4.3	Schmidt.
21	59	"	17	9 54	11	29.3	"	+9.7	"
22	61	Nov.	22	9 34	11	5.7	"	+6.1	"
23	"	"	"	"	9	30±	Greenwich.	+5	Knott.
24	65	Dec.	2	8 54	9	0	"	+15	"
25	"	"	"	"	10	25.8	Athens.	+6.2	Schmidt.
26	69	Dec.	12	8 14	9	47.7	"	+8.1	"
27	79	Jan.	6	6 34	6	36±	Greenwich.	+11	Knott.
28	92	Feb.	7	16 24	10	18.2	Cambridge.	+12.0	H. C. O.
29	96	"	17	15 44	9	37.2	"	+13.0	"
30	98	"	22	15 24	9	17.2	"	+13.0	"
31	110	March	24	13 24	7	16.4	"	+13.8	"
32	112	"	29	13 04	12	45	Greenwich.	+10	Knott.
33	114	April	3	12 44	12	24	"	+11	"
34	"	"	"	"	6	35.8	Cambridge.	+14.8	H. C. O.

All of the observations are compared in Table XIV. The columns give a current number, E or the number of minima which have elapsed since the discovery of the variability, the date, hour, and minute according to the approximate ephemeris used, and the observed minimum in mean time of the meridian of the observatory named in the fifth column. The last two columns give the correction to the ephemeris and the name of the observer. Observations made at the Harvard College Observatory are designated by H. C. O. Schmidt I. and Schmidt II. denote the two reductions referred to above.

For comparison with different ephemerides it will be convenient to group the observations of each observer, as has been done in Table XV. The observations of Dr. Schmidt in August according to his first and second reduction have been placed together, and also his later observations. The successive columns give a current number, the authority, the number of minima observed, and the mean value of E. The last four columns give the corrections in minutes to be applied to four ephemerides; that is, they equal the mean of the observed minus the computed value of each group according to the following four formulas:—

$$(A) \text{ Ep. E.} = 1880 \text{ June } 23^{\text{d}} 7^{\text{h}} 44.0^{\text{m}} + 2^{\text{d}} 11^{\text{h}} 50.0^{\text{m}} = E.$$

$$(B) \text{ Ep. E.} = 1880 \text{ June } 23^{\text{d}} 10^{\text{h}} 13.1^{\text{m}} + 2^{\text{d}} 11^{\text{h}} 44.94^{\text{m}} E. - 0.04376^{\text{m}} E^2.$$

$$(C) \text{ Ep. E.} = 1880 \text{ June } 23^{\text{d}} 8^{\text{h}} 12.0^{\text{m}} + 2^{\text{d}} 11^{\text{h}} 49.6^{\text{m}} E.$$

$$(D) \text{ Ep. E.} = 1880 \text{ June } 23^{\text{d}} 7^{\text{h}} 41.0^{\text{m}} + 2^{\text{d}} 11^{\text{h}} 49.9^{\text{m}} E.$$

The first of these formulas (A) is extremely convenient, since the minutes repeat themselves every six minima. As the period differs from two days and a half by exactly ten minutes, the times of the successive minima may be written down directly. Every two hundred and forty minima, or every five hundred and ninety-nine days, the hours and minutes repeat themselves, so that the ephemeris can be easily extended over long periods. Whatever ephemeris is adopted, it may be more convenient to compute the minima by this formula first and apply the difference of the ephemerides as a correction.

Formula (B) is derived from the law proposed by Dr. Schmidt on page 90 of his article, reducing to Paris mean time and adopting June 23 as the starting-point, as in the other ephemerides. A minimum is assumed to have occurred on December 7 at  $10^{\text{h}} 6.7^{\text{m}}$ , Athens mean time. The period at this time is taken as  $2^{\text{d}} 11^{\text{h}} 50.812^{\text{m}}$ , with an increase of 0.08753 in each successive period.<sup>a</sup> The ephemeris on page 91 is nearly, but not exactly, represented by this law. A part

of the discrepancy is due to an error by which the interval between the minima of October 3 and 6 is about five minutes too small. This will affect all the minima preceding or all of those following it. The number of decimal places employed by Dr. Schmidt has been retained, although the accuracy of the observations does not seem to justify it. Since we do not know the period within some tenths of a minute, it seems scarcely advisable to carry the result to thousandths of a minute in the formula used to represent it.

Formula (C) is proposed as that which best satisfies all the observations, if we admit that the period is invariable.

Formula (D) is that which best represents the later measures obtained at the Harvard College Observatory.

TABLE XV.—COMPARISON OF EPHEMERIDES.

No.	Authority.	No. Min.	E.	A.	B.	C.	D.
1	Glasenapp.	1	4	+22.0	-105.1	- 4.4	+25.4
2	Schmidt I.	5	20.0	+26.2	- 36.3	+ 6.2	+31.2
3	Schmidt II.	4	19.0	[+73.5]	+ 7.8	[+53.1]	+78.4
4	H. C. O.	2	38.0	+ 2.0	-14.6	-10.4	+ 8.8
5	Schmidt.	9	55.9	+ 8.1	+ 1.8	+ 2.5	+16.7
6	Knott.	5	61.4	+ 9.6	+ 1.5	+ 6.2	+18.7
7	H. C. O.	1	92	-12.0	- 65.7	- 3.2	+ 0.2
8	"	1	96	-13.0	- 79.0	- 2.6	- 0.4
9	"	1	98	-13.0	- 85.7	- 1.8	- 0.2
10	"	1	110	-13.8	-133.9	+ 2.2	+ 0.2
11	Knott.	1	112	-10	-137.2	+ 6.8	+ 4.2
12	"	1	114	-11	-149.7	+ 6.2	+ 3.4
13	H. C. O.	1	114	-14.8	-153.7	+ 2.8	+ 0.4

An examination of the residuals from Dr. Schmidt's formula shows that this ephemeris alone satisfies all of his measures, if we admit his second reduction of his observations in August. It, however, entirely fails to represent the later determinations. The deviations exceed two hours, both in the Harvard College measures and in those of Mr. Knott. When this ephemeris was published, these observations had not been made, and of course such a deviation could not have been foreseen. It is, however, remarkable that Dr. Schmidt should not have noticed the large discordance in the minimum observed by M. Glasenapp. This observation has especial value as a test of any ephemeris, since it is much earlier than any other measures. Dr. Schmidt's ephemeris would give a minimum at  $11^h 32^m$ , Moscow mean time, which is at once seen to be in error on inspecting Table XIII. or the original publication of M. Glasenapp. In fact, the reduction shows a correction to the time of minimum of over an hour and a half.

All the observations are fairly represented by formula (C), except the second reduction of those of Dr. Schmidt. His original reduction leaves a residual which might well be due to errors of observation. Although the residuals of the Harvard College measures are small, they are still much larger than their probable errors, and their values evidently indicate systematic error. The last formula satisfies these completely, giving average residuals of only 0.3 minutes, but does not agree with the other observations. If we admit a variation in the period, the value  $2^d 11^h 49.9^m$  would seem to be that between  $E = 90$  and  $E = 114$ , but not between  $E = 0$  and  $E = 90$ .

It is scarcely worth while at present to discuss the relative probability of these various formulas, since further observations which will doubtless soon be made will serve to decide between them with certainty. If the original observations were published, so that all could be reduced according to the same method, doubtless much greater accordance would be found in the results. There seems to be no reason why the error in determining each minimum from observation during the decrease and increase should not be reduced to two or three minutes or much less than those of  $\beta$  *Persei*. Should the discrepancy of certain measures, as those in August of Dr. Schmidt, be confirmed, they would indicate the existence of some disturbing body which might also account for such a deviation as that noted in the minimum of  $\beta$  *Persei* on Nov. 22. No correction has been applied for the aberration. The star is so near the pole of the ecliptic that the correction would never exceed two minutes, and would be masked by the other errors.

HARVARD COLLEGE OBSERVATORY,  
Cambridge, Mass.

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INVESTIGATIONS ON LIGHT AND HEAT, made and published wholly or in part with appropriation from the RUMFORD FUND.

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## XXII.

## ON THE GROUP "b" IN THE SOLAR SPECTRUM.

BY WILLIAM C. WINLOCK.

Presented by Prof. Wolcott Gibbs, June 9, 1880.

THE most complete charts of the solar spectrum now available are Kirchhoff's, which were published in 1861, and Ångström's, published in 1869. Kirchhoff employed a battery of four flint-glass prisms, with a collimator and observing telescope each of about 4 centim. aperture and 49. centim. focal length; while Ångström used telescopes of about 4.6 centim. aperture, and 36.3 centim. focal length, and a diffraction grating made by Nobert, containing about 133 lines to the millimetre.

Such great advances have been made very recently in the construction of optical instruments, and more especially in the ruling of diffraction gratings, that it would now be possible to enlarge Ångström's great chart almost as much as he improved upon Fraunhofer's first maps. But it would be an almost endless undertaking for a single observer to attempt a map of the whole spectrum, from the ultra-violet to the invisible red, brought to light by our most powerful instruments, and accordingly most physicists who have paid especial attention to solar spectroscopy have devoted themselves to a careful study of detached portions which appear of unusual interest. As a slight contribution to this work, the following observations upon the group of dark lines "b," of the solar spectrum, were undertaken at the suggestion of Dr. Gibbs, and carried on under his immediate supervision.

A table of wave-lengths, based upon the wave-lengths of Ångström's lines, has been computed, and, in addition to this, the wave-lengths of all new lines within the limits adopted, have been deduced by graphical interpolation, in order to give a check upon the values obtained for  $\lambda$  in the table on page 403.

The group "b" is readily distinguished about the middle of the green by its two bold components visible with very low dispersive



power, or by its three heavy and burred lines when seen under higher power. Its position near the brightest part of the spectrum, together with the readiness with which it can be recognized, make this group one of more than common interest. Moreover, since it combines, within very narrow limits, lines of almost every grade of heaviness and character, it would seem to have every qualification for a "test group" upon which the performance of any spectroscope may be tried. Indeed, for such a purpose it is equalled by few, and surpassed by no other groups of the spectrum.

The following is a brief description of the instruments employed:—

The spectroscope is mounted on a four-legged table, and the light is received through a circular aperture 11 centim. in diameter, from a "porte-lumière" fixed in a window upon the southern face of the building. The mirror of the *porte-lumière* is of silvered glass, and measures 10 centim. by 26 centim., and in this position can reflect the sunlight for about four hours only, during the day; that is, from 9 A.M. to 1 P.M. Before falling upon the slit of the collimating telescope, the light passes through a small cylindrical *condensing lens* measuring 4 centim. each way, with a focal length of 25.6 centim. This condenser is held in front of the slit by means of a wooden clamp. The *collimator* has an aperture of 4.76 centim., and focal length of 50 centim. The slit is 2.1 centim. long, and its width is adjustable by a rather coarse-threaded screw. The *observing telescope* is of 4.7 centim. aperture, and 49.6 centim. focal length. Three eyepieces can be used, and have been designated 1, 2, and 3. Their magnifying powers are approximately 35, 25, and 18 diameters. Both observing telescope and collimator admit of motion about two centres, so that proper adjustment can be made for any part of a grating, or for any number of prisms.

It was found that, owing to unsteadiness in the instrument, no accurate measurements could be made with the filar micrometer; so, abandoning the micrometer, a finely divided scale, with which all the measures were made, was placed in the highest power eyepiece. This method of measurement appears to possess all the accuracy attainable under the circumstances. The "eyepiece scale" was ruled by Professor W. A. Rogers upon a piece of glass 0.5 mm. in thickness, and 19 mm. diameter, cemented to a diaphragm at the focus of the eyepiece. The lines of the scale are seen with great distinctness, and, owing to the thinness of the glass upon which they are ruled, no appreciable amount of light is lost. Through the kindness of Professor Rogers I have been enabled to make a careful investigation of the

errors of this scale, and a determination of the values of its divisions. The results show that the maximum error in one division is 0.003 scale div., a quantity entirely insensible in the present investigation, since at best it is possible to estimate to hundredths of a division. The actual value of one division is  $\frac{1}{19.7}$ th of an inch = 0.053 of a millimetre.

During the progress of the work two ends were held in view: First, to obtain data for comparing the appearance of the group under different conditions of the atmosphere, of dispersive power, etc.; and secondly, to measure the positions, and thus determine the wave-lengths of all lines seen with certainty within the assumed limits. For the first purpose mentioned, an enlarged copy of Ångström's chart was prepared, and below this were roughly sketched, on the various days of observation, the lines which were seen, — the grating and power being noted in the margin. All lines which could be measured were afterwards accurately entered upon the chart, and those which were not seen a second or third time were entered by estimation. In this way I obtained twenty-three observations of the group, between November, 1879, and May, 1880, using eight diffraction gratings and two prisms. Four of the gratings were ruled by Rutherford, of 17,296, 8,640, 13,321, and 7,021 lines per inch respectively; three by Professor Rogers, of 2,540, 2,540, and 5,080 lines per inch; one by Brunner, of 2,540 lines per inch. Grating 17,296 is on speculum metal, the ruled surface measuring 4.3 centim. in length by 4.8 centim. in width. Observations were usually made upon the spectrum of the second order. Dispersive power = 1860. Grating 13,321, silvered glass. Grating 7,021, on speculum metal covered with glass. The three gratings of 2,540 lines were ruled upon glass prepared by Brunner Frères, and were used for transmitted spectra. Grating 5,080 was ruled upon ordinary "commercial crystal" glass, and seems far superior to several gratings ruled upon better quality of glass, and showing less error in the spacing and cut of the lines. This grating was also used for transmitted spectra. A comparison of the three 2,540 gratings seems to show that those ruled by Professor Rogers are fully equal, if not superior, to Brunner's.

In the preparation of the chart given in Plate II, Rutherford's grating of 8,640 lines was used. This is ruled upon speculum metal with the following memorandum upon its edge: — "Aug. 2, 1877, 8,640 per in., 17,640 spaces. Man'd by D. C. Chapman with Mr. Rutherford's Engine. 175, 2 Ave., N. Y." The length of the lines is 4.3 centim., and the width of the ruled surface 5.2 centim. As far as working

power is concerned, this grating seemed better than the one of 17,296 lines per inch, — at least under ordinary conditions of the atmosphere. For the dispersive power\* we shall have, according to the formula given by Professor Pickering (vol. xi. (n. s. iii.), p. 273, Proc. Am. Acad.),

$$\frac{dr}{d\lambda} = \frac{(340)(3)}{.719} = 1419,$$

the observations being made upon the third order of spectrum with an angle of reflection of 44°.

To determine the wave-lengths of the thirty-seven lines given in Plate II., it was only necessary to note the position of each line upon the "eyepiece scale," and, having found the value of a division of the scale in wave-lengths, to reduce the scale readings to wave-lengths and add them to the wave-length of the line upon which the zero of the scale was set. In this way the absolute wave-lengths were made to depend, practically, upon the wave-length of the initial line, as assumed from Ångströms chart.

It was a matter of no small difficulty to decide upon the positions of some lines, owing to their excessive faintness, and discrepancies in the readings are not to be wondered at. A few preliminary measurements were found to be somewhat discordant, but this was probably due to parallax in the scale, which was discovered a little out of focus. I concluded, therefore, that the most accurate results would be obtained by employing a set of measurements all made on the same day, since relative positions only were required. On May 15, 1880, five independent sets of readings were made, each set including the whole number of lines to be measured.

The first line of the scale was set upon the line designated  $b^1$ , by the aid of a slow motion screw, and the readings of the different lines up to  $b^{37}$  noted by estimation to hundredths of a division. A single reading cannot be relied upon within, perhaps, one-tenth of a division, but in some cases it seemed advantageous to attempt a closer estimation. Ten readings of the lines  $b^6$ ,  $b^{14}$ ,  $b^{33}$ , and  $b^{37}$  were made. The probable error of a single reading of  $b^{37}$  is  $\pm .014$  div., and the probable error of the mean of ten readings  $\pm .005$  div. Where but five readings were made, as, for instance,  $b^{13}$ , the probable error of a single observation is  $\pm .028$ , and the probable error of the result  $\pm .013$  scale divisions, corresponding to 0.011 tenth metres.

---

\* Ångström used dispersive powers of 665 and 798.

If, then, we put

$\lambda_0$  = the wave-length of the initial line  $b^1$

and  $\lambda_x$  = the wave-length of a line whose reading upon the scale is  $x$ ,

we shall have

$$\lambda_x - \lambda_0 = x \rho$$

where  $\rho$  is a constant factor (the equivalent in wave-lengths of one division of the scale), which must be obtained from the lines of known wave-length (i. e.,  $\lambda_x$  given), by the relation

$$\rho = \frac{\lambda_x - \lambda_0}{x}$$

or, putting for convenience

$$\lambda_x - \lambda_0 = \Delta \lambda$$

we have

$$\rho = \frac{\Delta \lambda}{x}$$

and

$$\Delta \lambda = x \rho.$$

For the determination of  $\rho$  I have used the wave-lengths of all lines given by Ångström, except  $b^3$  and  $b^5$ , and for these Ångström gives but a single value, 5164.59, which appears to be about their mean wave-length. The mean of fifteen values of  $\rho$  thus obtained is

$$\rho = 0.85476 \quad \log \rho = 9.93184$$

How nearly this value satisfies each of the lines by means of which it was obtained, may be seen by comparing the last two columns in the table upon page 403.

Having found  $\rho$ , the wave-length,  $\lambda_x$ , of any unknown line is readily determined, for we see

$$\lambda_x = \lambda_0 + x \rho,$$

or

$$\lambda_x = \lambda_0 + \Delta \lambda.$$

This last quantity,  $\lambda_0 + \Delta \lambda$ , is found on page 403, and the corresponding " $\lambda$ " of Ångström's lines are given in the next column. All wave-lengths are expressed in "tenth-metres," a tenth-metre being  $\frac{1}{10^{10}}$  of a metre: for instance, the wave-length of  $b^1$  is

$$0.000000516162 \text{ metre.}$$

Taking for abscissas the readings,  $x$ , of the scale, and for ordinates the wave-lengths of the corresponding lines as given by Ångström, a "curve of wave-lengths" was drawn through the points found. The wave-lengths thus graphically deduced were found to agree closely

with those computed in the table below. The "intensity" or heaviness of the lines has been estimated roughly by the eye, taking the intensity of  $b^1$  as unity. The mean of three separate estimations is given upon the next page, and these intensities have been used in forming the chart, Plate II. For convenience the wave-lengths  $\lambda$ , and intensities I. are placed together in a table upon page 404.

TABLE OF WAVE-LENGTHS:—GROUP "b."

Line.	I.	II.	III.	IV.	V.	Mean ( $\bar{x}$ )	$\Delta \lambda$	$\lambda x = \lambda_0 + \Delta \lambda$	$\lambda$ Ångström.
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5161.62	5161.62
2	0.80	0.80	0.70	0.90	0.70	0.78	0.67	62.29	
3	2.78	2.70	2.75	2.75	2.80	2.76	2.36	63.98	
4	8.10	8.10	8.08	8.10	8.10	8.10	2.65	64.27	
5	3.80	8.65	8.80	3.75	8.80	3.76	3.21	64.83	
6	4.75	4.70	4.80	4.75	4.80	4.76	4.07	65.69	65.74
7	5.00	5.00	5.00	5.00	5.00	5.00	4.27	65.89	
$b_4$ 8	6.01	6.09	6.03	6.03	6.03	6.04	5.16	66.78	66.75
9	7.60	7.45	7.45	7.40	7.40	7.46	6.38	68.00	
$b_3$ 10	7.97	7.90	7.90	7.90	7.90	7.91	6.76	68.38	68.34
11	8.10	8.05	8.10	8.10	8.10	8.09	6.91	68.53	
12	9.90	9.90	9.90	9.94	9.90	9.91	8.47	70.09	
13	10.00	10.03	10.08	10.08	10.10	10.06	8.60	70.22	
14	10.98	11.00	10.98	10.97	11.00	10.99	9.39	71.01	71.06
$b_2$ 15	12.00	12.10	12.10	12.10	12.10	12.08	10.32	71.94	72.02
16	13.10	13.19	13.20	13.20	13.20	13.18	11.26	72.88	
17	16.10	16.00	16.00	16.10	16.00	16.04	13.71	75.33	
18	16.90	16.95	16.75	16.80	16.77	16.83	14.39	76.01	75.59
19	17.40	17.40	17.40	17.40	17.40	17.40	14.87	76.49	76.38
20	17.70	17.75	17.65	17.75	17.70	17.71	15.14	76.76	
21	19.20	19.10	19.10	19.10	19.10	19.12	16.34	77.96	78.13
22	19.65	19.78	19.75	19.80	19.65	19.73	16.86	78.48	
23	20.95	20.90	20.90	20.85	20.90	20.90	17.86	79.48	79.52
24	22.10	22.18	22.10	22.10	22.10	22.12	18.91	80.53	
25	22.90	22.90	23.00	22.95	22.90	22.93	19.60	81.22	
$b_1$ 26	25.00	24.98	24.98	24.98	24.98	24.98	21.35	82.97	82.96
27	25.83	25.70	25.80	25.70	25.65	25.77	22.03	83.65	
28	25.98	26.00	25.98	25.98	25.99	25.99	22.21	83.83	
29	27.80	27.60	27.50	27.45	27.40	27.43	23.45	85.07	85.10
30	28.10	28.20	28.20	28.10	28.20	28.16	24.07	85.69	
31	29.80	29.90	29.97	29.90	29.95	29.90	25.56	87.18	87.35
32	30.10	30.10	30.10	30.10	30.10	30.10	25.73	87.35	
33	31.00	30.97	31.00	31.00	31.00	30.99	26.49	88.11	88.18
34	31.90	32.00	31.80	31.90	31.80	31.88	27.25	88.87	
35	34.03	34.05	34.10	34.00	34.00	34.04	29.10	90.72	90.53
36	34.97	34.90	34.70	34.70	34.80	34.81	29.75	91.37	
37	35.10	35.10	35.10	35.10	35.08	35.10	30.00	5191.62	5191.65

TABLE OF WAVE-LENGTHS AND INTENSITIES:—GROUP "b."

Line.	I.	$\lambda$	Line.	I.	$\lambda$
1	1.0	5161.62	20	0.2	5176.76
2	0.1	62.29	21	0.4	77.96
3	0.6	63.98	22	0.2	78.48
4	0.4	64.27	23	0.7	79.48
5	0.8	64.83	24	0.3	80.53
6	0.9	65.69	25	0.1	81.22
7	0.1	65.89	26	2.7	82.97
8	2.9	66.78	27	0.3	83.65
9	0.2	68.00	28	0.3	83.83
10	1.6	68.38	29	0.7	85.07
11	0.1	68.53	30	0.3	85.69
12	0.2	70.09	31	0.6	87.18
13	0.2	70.22	32	0.1	87.35
14	1.0	71.01	33	1.7	88.11
15	2.7	71.94	34	0.1	88.87
16	0.9	72.88	35	1.6	90.72
17	0.1	75.33	36	0.1	91.37
18	0.7	76.01	37	1.6	5191.62
19	0.2	5176.49			

Plate I. At the head appears Ångström's chart of the group, enlarged four times. A map quite similar to this plate was prepared and upon it was sketched, each day, the appearance of the group as seen with the particular grating employed. The position of any new line was estimated from its relation to those adjoining, and the eyepiece scale was not used. The date, grating, power of eyepiece, number of lines seen, and order of spectrum, whenever noted, are given in the margin. The two sketches given on Dec. 17, 1879, were made with the help of a large collimating telescope of 6.7 centim. aperture, and 1.62 centim. focal length, but it appeared to possess little, if any, advantage over the shorter collimator. On Jan. 2, 1880, the chart was made from one flint glass and one bisulphide of carbon prism, each prism having a refracting angle of  $60^\circ$ . Where two lines were not separated by the 2540 gratings, I have indicated the fact by blending them upon the chart; and where there was any question as to the visibility of a line, an interrogation mark has been placed opposite.

Plate II. gives the final determination of the "b" Group upon a scale four times that of Ångström, and also shows the group as given in the charts of Kirchhoff and Ångström, the scale being unaltered in either case. Ångström gives 20, Kirchhoff 17 lines. The chart contains all the lines given by Ångström, together with such additional

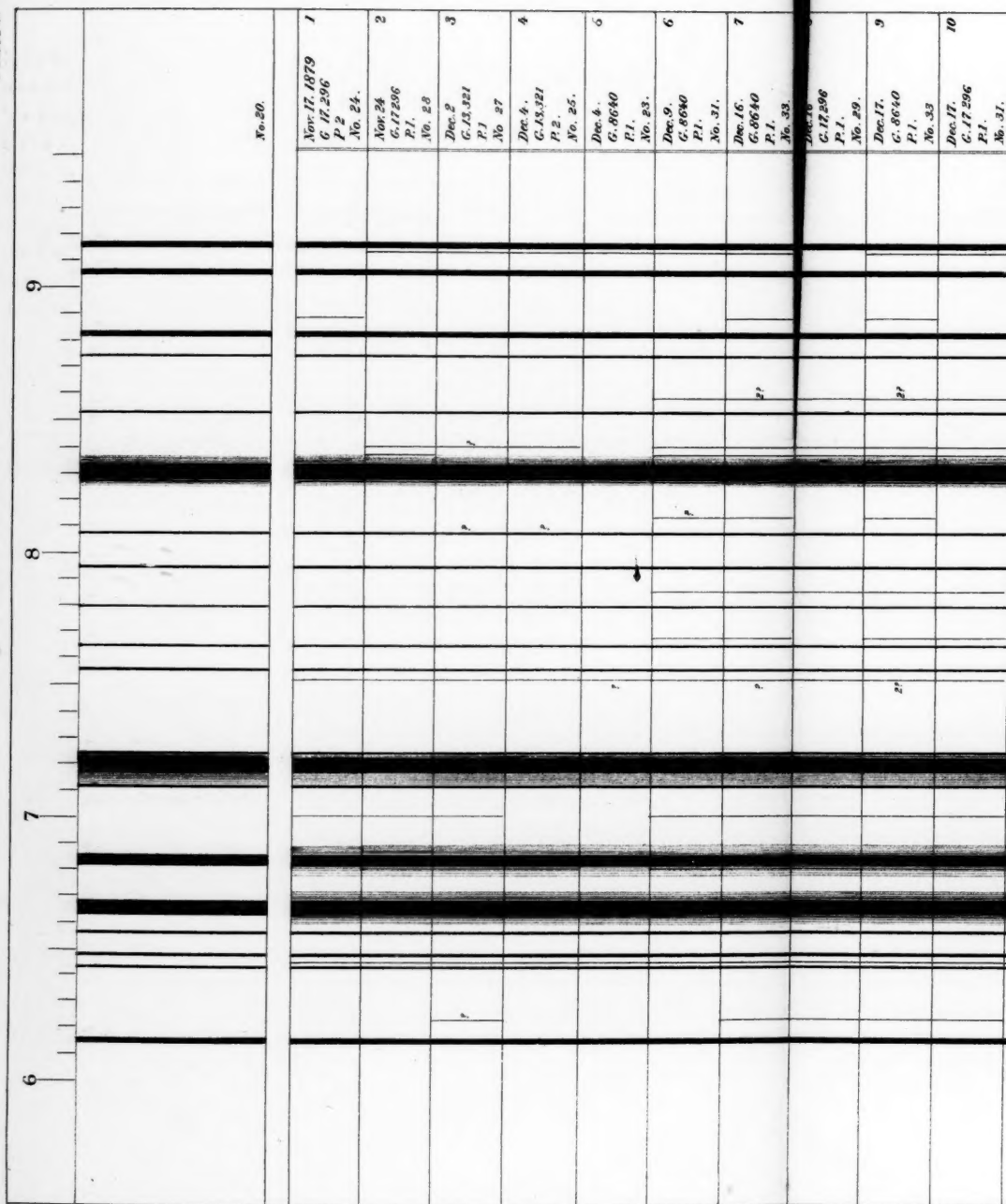
lines as it was possible to measure. The limits of the group were assumed arbitrarily, and the lines numbered from 1 to 37 inclusive. To avoid confusing lines thus designated with those called by Ångström  $b_1, b_2, b_3, b_4$ , it will be necessary to write these figures above the line, as  $b^5, b^{32}$ , etc. It might be noticed here that each of the lines  $b^1$  and  $b^{37}$  has a faint "companion" or component just outside the limits adopted, and therefore not shown. Wave-lengths can be read directly from the chart, to the tenth part of a tenth-metre, by estimating to tenths upon the scale, and suffixing the three figures thus obtained to 51:—for instance, the wave-length of  $b^1$  will be

5164.3 tenth metres.

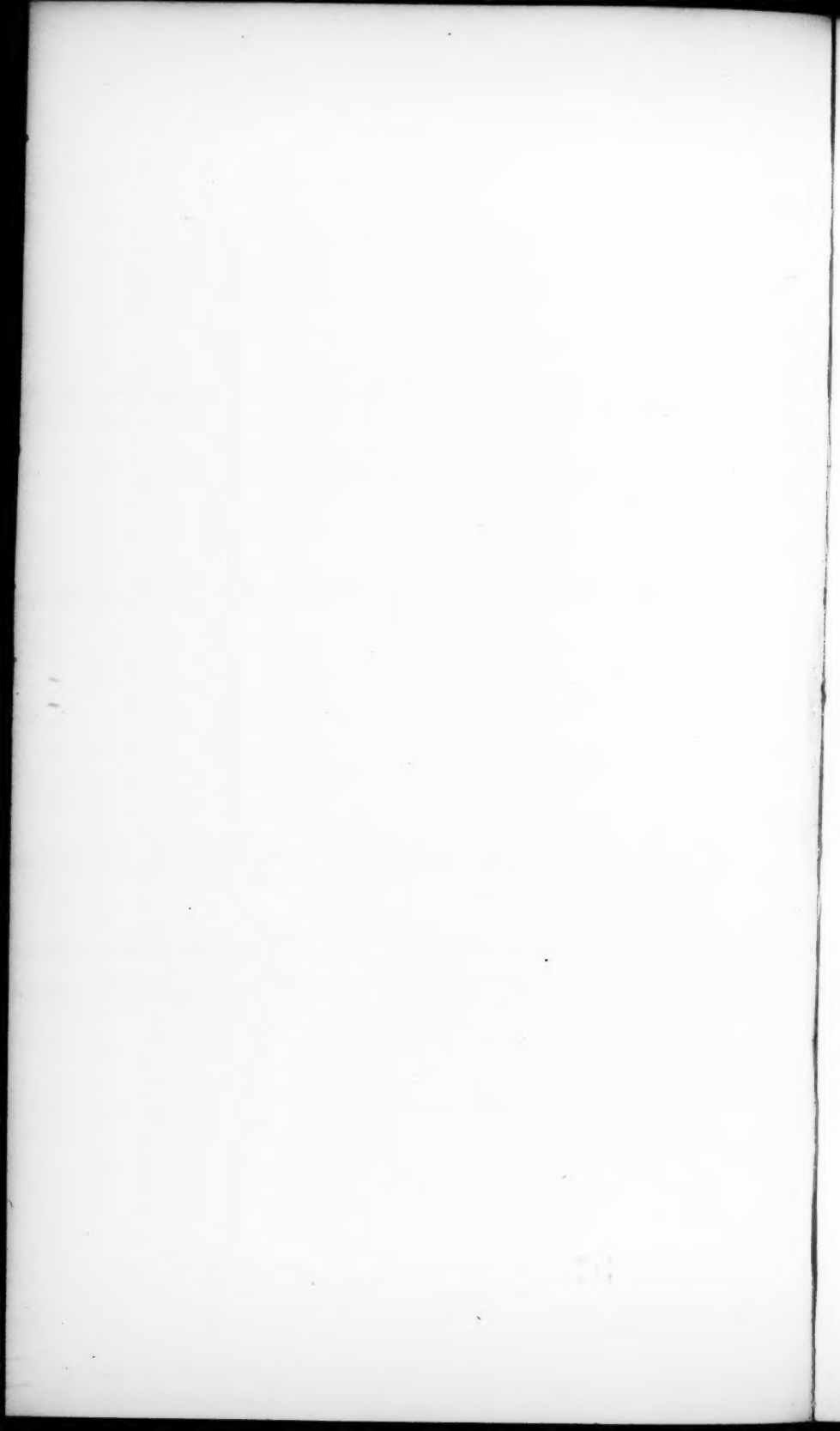
The relative intensity and character of the lines are represented as faithfully as possible; though it has been found exceedingly difficult to give any very good idea of the peculiar *blurred* or *burred* appearance so noticeable in the lines  $b_1, b_2$ , and  $b_4$ .



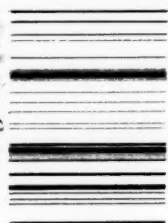
# Plate I.



[illegible]

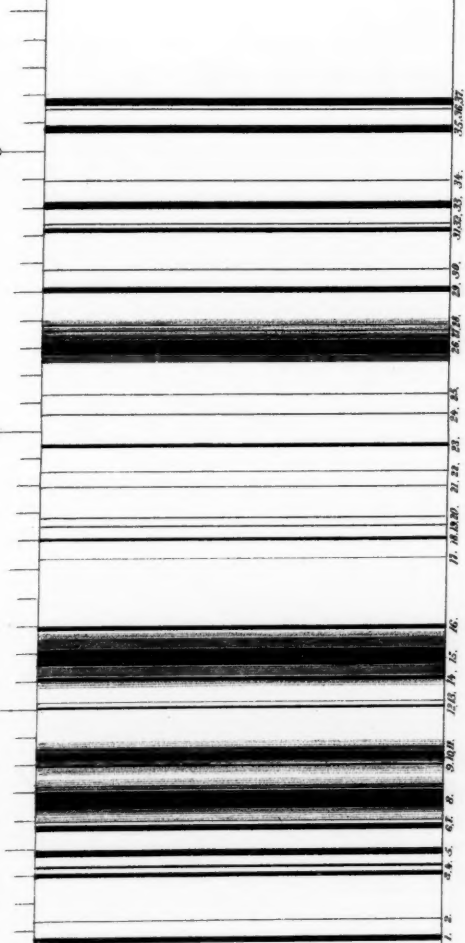


*Angström.*

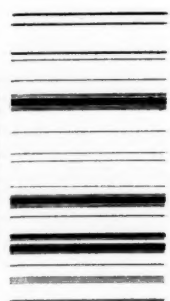


"b" Group.

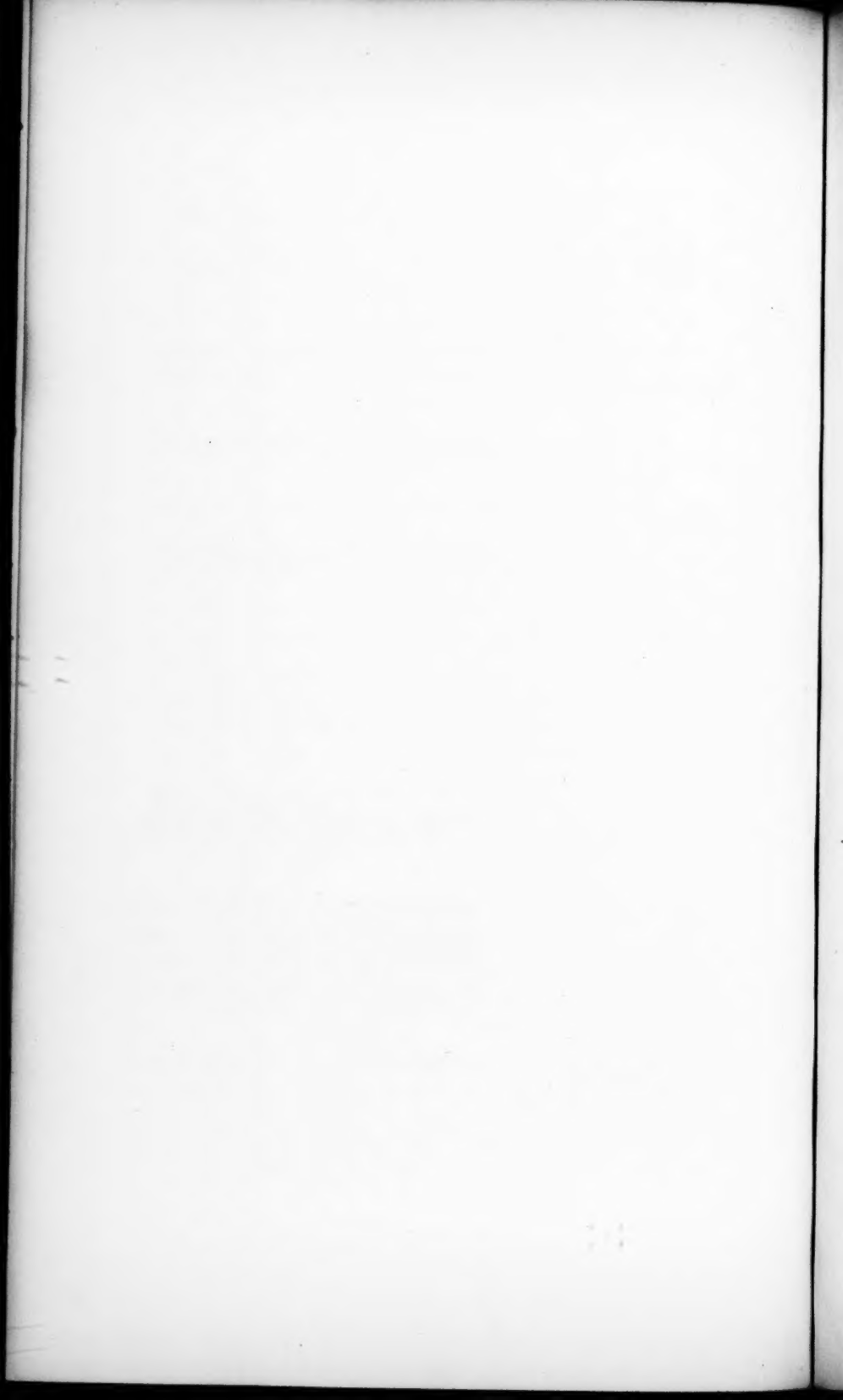
6 7 8 9



*Kirchhoff.*



1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34.



## PROCEEDINGS.

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Seven hundred and thirty-second Meeting.

May 25, 1880. — ANNUAL MEETING.

The VICE-PRESIDENT in the chair.

The Treasurer and Librarian presented their annual reports.

Professor Lovering presented the following report from the Rumford Committee : —

“The mechanical theory of heat, which treats of heat as being, not a peculiar kind of matter called caloric, but as being some form or forms of molecular motion, has made necessary and possible a new branch of mechanics, under the name of thermo-dynamics. This theory has not only introduced new ideas into science, but has demanded the application, if not the invention, of special mathematical equations. Clausius has devoted thirty years to the development of thermo-dynamics, and at the end of his ninth memoir he expresses, in two brief sentences, the fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat: 1. The energy of the universe is constant; 2. The entropy of the universe tends towards a maximum.

“Professor J. Willard Gibbs, in his discussion of the ‘Equilibrium of Heterogeneous Substances,’ derives his criteria of equilibrium and stability from these two theorems of Clausius, and places the two generalizations of Clausius in regard to energy and entropy at the head of his first publication. Having derived from his criteria some leading equations, and having defined his sense of ‘homogeneous’ and its opposite, he applies these equations : —

“1. To the internal stability of homogeneous fluids.

“2. To heterogeneous masses, under the influence of gravity or

otherwise; such as gas-mixtures, solids in contact with fluids, osmotic forces, capillarity, and liquid films.

"3 Finally, he considers the modifications introduced into the conditions of equilibrium by electromotive forces.

"His treatment of the subject is severely mathematical, and incapable of being translated into common language. The formulas, however, are not barren abstractions, but have a physical meaning.

"The laws of thermo-dynamics reach down to the heart of physics and extend their roots in all directions. It is now understood that the energy of a system of bodies depends on the temperature and physical state, as well as on the forms, motions, and relative positions of these bodies. The Rumford Committee congratulate the Academy on the opportunity they now enjoy of awarding the Rumford Premium for a contribution to physical science of far-reaching importance; not anticipating, but already realizing, the approval which this award must receive from all who are conversant with the subject.

"For the Committee,

"JOSEPH LOVERING, *Chairman.*"

The report concluded with the recommendation of the following vote, which was unanimously adopted:—

"*Voted*, That the Rumford Premium, consisting of a gold and silver medal, be awarded to Professor J. Willard Gibbs for his researches in thermo-dynamics; and that the Treasurer be authorized to pay for the same from the income of the Rumford Fund."

On the motion of Professor Gray, it was

*Voted*, That the election of officers be postponed until the adjourned meeting.

On the motion of Professor Cooke, it was

*Voted*, That, when the Academy adjourn, it adjourn to the second Wednesday in June; and that the election of officers take place at that meeting.

On the motion of Professor Cooke, it was

*Voted*, That five hundred dollars (\$500) of the unexpended balance for last year be appropriated for the publication of the forthcoming volume of Proceedings.

On the motion of Mr. Seudder, it was

*Voted*, That three hundred and fifty dollars (\$350) from



the unexpended balance for last year be appropriated to complete the binding of books now in the hands of the binder.

The Treasurer, the Corresponding Secretary, and the Librarian were appointed a committee on appropriations for the coming year.

The following gentlemen were elected members of the Academy:—

John Rayner Edmands, of Cambridge, to be a Resident Fellow in Class I., Section 2.

Henry Purkitt Kidder, of Boston, to be a Resident Fellow in Class III., Section 3.

Marcelin Pierre Eugène Berthelot, of Paris, to be a Foreign Honorary Member in Class I., Section 3, in place of the late James Clerk Maxwell.

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Seven hundred and thirty-third Meeting.

June 9, 1880. — ADJOURNED ANNUAL MEETING.

The VICE-PRESIDENT in the chair.

The death was announced of Dr. C. A. F. Peters, Director of the Kiel Observatory.

A letter was read from the Honorable Charles Francis Adams, announcing his resignation of the office of President of the Academy.

The following votes were proposed by Professor Asa Gray and unanimously adopted:—

*Voted*, That the Academy receives with much regret the announcement from the Honorable Charles Francis Adams that the state of his health obliges him to decline further service as President of this society.

*Voted*, That the Fellows of the Academy deeply regret that their distinguished President found himself unable to be present at the Centennial Celebration on the 26th ult., to deliver the historical discourse which he had prepared in compliance with the Academy's invitation; and they respectfully

solicit from Mr. Adams the manuscript of this discourse, in order that it may be published along with the addresses which were pronounced on that interesting occasion.

*Voted*, That the Fellows of the Academy desire to place upon record their grateful sense of the great value of their late President's services for the seven years in which he has filled the chair formerly occupied by his illustrious father and grandfather; and they proffer their best wishes for the restoration of his health in the respite from official duties which he finds it needful to seek.

On the motion of President Eliot, it was

*Voted*, That the thanks of the Academy be presented to the committee which made the excellent arrangements for the celebration of the Academy's hundredth anniversary on May 26th, and particularly to the Honorable Robert C. Winthrop for the very interesting and appropriate address which he delivered on the occasion, in the unexpected absence of the President.

The following report was read: —

*Report of the Rumford Committee.*

"Since the last annual report, Professor Rowland's elaborate investigation in relation to the mechanical equivalent of heat has been completed, and the results are printed at length in the current volume of Proceedings.

"The experiments of Mr. Holman, under the direction of Professor Cross, on the viscosity of gases, have been continued, but are not yet ready for publication.

"Other researches are in progress by members of the Committee or under their direction: those of Dr. Gibbs on measurements with the spectrometer; those of Professor Trowbridge on the heat developed by the magnetizing and demagnetizing of metals; and those of Mr. Edmands on atmospheric refraction.

"The Committee, with the consent of the Academy, took advantage of an opportunity not likely to occur again, for obtaining a copy of the standard metre of the French Government.

"They have also had the satisfaction of seeing their recommendation of the Rumford Premium to Professor J. Willard Gibbs approved by the Academy.

"They request that an appropriation of \$500 be made from the income of the Rumford Fund, to enable them to continue the researches upon light and heat.

"All which is respectfully submitted.

"For the Committee,

"JOSEPH LOVERING, *Chairman*.

"JUNE 9, 1880."

In accordance with the recommendation of the Rumford Committee, it was

*Voted*, That an appropriation of five hundred dollars (\$500) be made from the income of the Rumford Fund to enable the Rumford Committee to continue the researches upon light and heat.

On the motion of the Treasurer, it was

*Voted*, To appropriate, —

|                                |            |
|--------------------------------|------------|
| For publication . . . . .      | \$1,100.00 |
| For library . . . . .          | 700.00     |
| For general expenses . . . . . | 2,200.00   |

The following papers were presented by title: —

"Botanical contributions: Characters of new Genera and Species of Plants of North America and Mexico." By Asa Gray.

"On the Dimensions of the Fixed Stars, with Especial Reference to Binaries and Variables of the Algol Type." By E. C. Pickering.

1. "Furfurol, a Product of the Dry Distillation of Wood."  
2. "Pyroxanthine." 3. "Mucobromic Acid and Certain of its Derivatives." By Henry B. Hill.

"Contributions from the Physical Laboratory of Harvard University." By John Trowbridge.

1. "Effect of Tension upon the Vibration of thin Membranes."
2. "Magnetic Constant of Fleitman's Nickel."
3. "Thermal Conductivity of Poor Conductors."
4. "Crooke's Phenomena in Ordinary Air."
5. "Earth Currents."

The annual election resulted in the choice of the following officers:—

JOSEPH LOVERING, *President*.  
 OLIVER W. HOLMES, *Vice-President*.  
 JOSIAH P. COOKE, *Corresponding Secretary*.  
 JOHN TROWBRIDGE, *Recording Secretary*.  
 THEODORE LYMAN, *Treasurer*.  
 SAMUEL H. SCUDDER, *Librarian*.

*Council.*

JAMES M. PEIRCE,  
 JOHN M. ORDWAY, } of Class I.  
 WOLCOTT GIBBS,

ALEXANDER AGASSIZ,  
 HENRY W. WILLIAMS, } of Class II.  
 GEORGE L. GOODALE,

ROBERT C. WINTHROP,  
 CHARLES G. LORING, } of Class III.  
 FRANCIS J. CHILD,

*Rumford Committee.*

WOLCOTT GIBBS, JOHN TROWBRIDGE,  
 EDWARD C. PICKERING, JOSIAH P. COOKE,  
 JOHN M. ORDWAY, JOSEPH LOVERING,  
 GEORGE B. CLARK.

*Member of Finance Committee.*

THOMAS T. BOUVÉ.

The following committees were appointed by the President:—

*Committee on Publication.*

JOSIAH P. COOKE, ALEXANDER AGASSIZ,  
 JOHN TROWBRIDGE.

*Committee on Library.*

EDWARD C. PICKERING,      HENRY P. BOWDITCH,  
WILLIAM R. NICHOLS.

*Auditing Committee.*

HENRY G. DENNY,      ROBERT W. HOOPER.

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Seven hundred and thirty-fourth Meeting.

October 13, 1880. — STATED MEETING.

The PRESIDENT in the chair.

The President announced the death of Professor Haldeman, Count Pourtalès, Dr. C. T. Jackson, and Professor Benjamin Peirce.

The Corresponding Secretary announced that letters had been received from Mrs. Miller, announcing the death of Professor William Hallows Miller; M. Berthelot, acknowledging election as Foreign Honorary Member; and Mr. Theodore Lyman, announcing the death of Count Louis François de Pourtalès.

The following gentlemen were elected members of the Academy: —

Henry Williamson Haynes, of Boston, to be a Resident Fellow in Class III., Section 2.

Arthur Auwers, of Berlin, to be a Foreign Honorary Member in Class I., Section 2, in place of the late Christian August Friedrich Peters.

Alfred Louis Olivier Legrand des Cloizeaux, of Paris, to be a Foreign Honorary Member in Class II., Section 1, in place of the late William Hallows Miller.

Professor Pickering presented, by title, the following papers: —

“Determination of the Greatest Height, consistent with Stability, that a Vertical Pole or Mast can be carried, and of the Greatest Height to which a Tree can Grow.” By A. G. Greenhill.

"Theory of the Constitution of the Sun, founded upon Spectroscopic Observations, original and other." By Charles S. Hastings.

Mr. S. H. Scudder exhibited a remarkable fossil insect. Remarks upon this subject were made by Professor Morse.

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Seven hundred and thirty-fifth Meeting.

November 10, 1880. — MONTHLY MEETING.

The PRESIDENT in the chair.

The President, in the absence of the Corresponding Secretary, read letters from Mr. Henry W. Haynes, accepting fellowship in the Academy, and the Honorable Charles Francis Adams, relative to the address which he prepared for the recent centennial of the Academy.

The following papers were presented: —

"On the Nomenclature of various Manifestations of Energy." By A. E. Dolbear.

"On an Acoustic Phenomenon noticed in a Crooke's Tube." By Charles R. Cross.

Professor Dolbear spoke of a possible means of protection from lightning.

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Seven hundred and thirty-sixth Meeting.

December 8, 1880. — MONTHLY MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read letters from Messrs. Auwers and Des Cloizeaux, acknowledging election as Foreign Honorary Members; M. Daguin, presenting a copy of the fourth edition of his *Traité de Physique*; and C. N. Racotta, President, announcing the formation of the "Société d'Agriculture Roumaine," at Bucharest, and proposing an exchange of publications with the Academy.

The following papers were presented :—

“Superficial Tension at Low Temperatures.” By N. D. C. Hodges.

“Palæozoic Myriapods as Types of a New Order.” By S. H. Scudder.

“Relation between the Imperial Yard, Bronze No. 1, and the Metre of the Archives.” By W. A. Rogers.

“On the Conditions for Accuracy in Measuring the Angle between two Reflecting Surfaces.” By J. Rayner Edmands.

The Recording Secretary read the following paper :—

“On the Distribution of Heat in the Diffraction Spectrum.” By S. P. Langley.

Remarks on this paper were made by Professors Cooke and Dolbear.

The following papers were presented by title :—

“On Chlorbromacrylic Acids and Diiodbromacrylic Acid.” By C. F. Mabery and Rachel Lloyd.

“Memoir on Phosphorescence.” By John W. Draper.

Professor Dolbear read the following papers :—

“On the Physical Theory of Gravitation.”

“On the Amplitude of Atomic Motions.”

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Seven hundred and thirty-seventh Meeting.

January 12, 1881. — STATED MEETING.

The Academy met at the house of Mr. Henry P. Kidder, 2 Newbury Street, Boston.

The President opened the meeting with the following address :—

“In a letter, dated July 12, 1796, addressed to the Hon. John Adams, then President of the Academy, Count Rumford gave notice of the trust which he had committed to their administration. Since 1797, when the funds indicated in this letter were received, the Academy has not failed in earnest endeavors to comply with the conditions of the trust. At the annual meeting of 1799, it was voted that the



terms on which the Rumford Premium, thus instituted, might be awarded should be published in the newspapers of the Capitals of the different States and of some of the American Islands. At the annual meeting of 1801 it was voted, that the Academy, at their meeting in May next, and afterwards biennially, will decide on the discovery or improvement which may appear to be entitled to the premium contemplated by Count Rumford, according to the terms of his letter of July 12, 1796. In 1802, a committee of the Academy reported that no discovery or improvement worthy of the premium, and fulfilling the required conditions, had come to their knowledge. In 1804, a claim was presented which did not receive the approval of the Academy. In 1805, it was voted that the terms on which the premium might be awarded should be published annually. In 1806, two more unsuccessful claims were presented. In 1809, a committee consisting of Judge John Davis, the Hon. John Quincy Adams, with the Recording Secretary, was appointed to consider generally the question of the Rumford Premium. In 1811, it was voted that the Secretary should publish a description of the Rumford Trust. In 1816, it was again voted that the conditions attached to the premium should be published annually. Another vote to the same effect was passed in 1820. In 1824, several applications were referred to a committee, and were probably included in the five applications rejected in 1830.

"It thus appears that the failure of the Academy to make any award, during this long period, cannot be charged to any lack of interest or attention on the part of our predecessors. It was partly due to the low state of some branches of physical science at that time; but also, in part, to some of the conditions under which the trust had been given and received. In consequence of a long report upon the subject made to the Academy in 1829, by a distinguished committee, consisting of Nathaniel Bowditch, Josiah Quincy, and Francis C. Gray, relief in the matter of the Rumford Fund was sought in 1831, and obtained in 1832, from the Supreme Court of Massachusetts. With the greater freedom of administration thus acquired, the Academy has been able to award the Rumford Premium nine times, eight of which have occurred since 1861, as follows:—

- "1. To Robert Hare, for the Compound Blowpipe.
- "2. To John B. Ericsson, for Improvements in the Caloric Engine.
- "3. To Daniel Treadwell, for Improvements in the Construction of Cannon.
- "4. To Alvan Clark, for Improvements in Achromatic Telescopes.

- "5. To George H. Corliss, for Improvements in the Steam-engine.
- "6. To Joseph Harrison, Jr., for his Method of constructing Steam-boilers.
- "7. To L. M. Rutherford, for Improvements in Astronomical Photography.
- "8. To John W. Draper, for his Researches on Radiant Energy.
- "9. To J. Willard Gibbs, for his Researches in Thermo-dynamics.

"The medals which were awarded to Professor J. Willard Gibbs at the last annual meeting of the Academy, have been prepared under the direction of the Rumford Committee, and are now ready for presentation.

"Rumford lived at a time when the machinery of science was largely composed of supernumerary fluids, interpenetrating or superimposed upon ordinary matter. Newton had indeed banished from mechanical astronomy the celebrated vortices of Descartes; but Franklin and others had introduced a fresh supply of hypothetical fluids into the sciences of electricity, magnetism, and heat. Many of us are old enough to have witnessed a great and pregnant revolution in thermotics; when the theory that heat is a mode of motion supplanted the old view that heat is an impalpable substance,—the caloric, that is, of Rumford's day. Since the establishment of the new view, many anticipations of it, which produced no impression upon science at the time, have been rescued from oblivion. In a lecture read in the chapel of Harvard College, on Nov. 26, 1755, on occasion of the great earthquake which shook New England the week before, Professor John Winthrop said: 'There seems to be an inexhaustible source of this heat in the attractive powers which Sir Isaac Newton has shown to belong to the particles of matter; for heat, consisting of a peculiar intestine motion of the parts of bodies, whatever tends to produce this motion in bodies will cause them to grow hot. Now such a motion may be produced by the particles of different bodies rushing together in virtue of their attractive powers.' The philosopher Locke held the same view, and expressed it elegantly, thus: 'What in our sensation is *heat*, in the object is nothing but motion.' Bacon's definition of heat antedates all this, and is no less explicit. His words are: 'When I say of motion that it is the genus of which heat is a species, I would be understood to mean, not that heat generates motion, or that motion generates heat (though both are true in certain cases), but that heat itself, its essence and quiddity, is motion, and nothing else. . . .'

"But all these preconceived suggestions of the reasoning faculty are,

in a scientific point of view, overshadowed by the grand experiment of Rumford, made at Munich in 1798, when, in the process of boring cannon, he converted, by the agency of what has been vaguely called friction, mechanical power into heat, and on a scale sufficient to boil two and one half gallons of water; and saw, with his clear, scientific vision, that nothing could have been excited or communicated by this operation but some kind of motion. Less dazzling, but no less conclusive, was Davy's later experiment of melting ice by rubbing. But the views of Rumford were in advance of the general scientific thought of his day by more than a generation, and were finally forced upon science by the long and masterly series of experiments made by Joule. The rude data supplied by Rumford's experiment gave, in the hands of Joule, an approximate value to the mechanical equivalent of heat; but our knowledge of the precise rate of exchange in the mutual conversion of heat and power rests upon the repeated, varied, and elaborate experiments of Joule himself. I will now let Mr. Tyndall speak for Rumford. 'When,' he says, 'the history of the dynamical theory of heat is written, the man who, in opposition to the scientific belief of his time, could experiment, and reason upon experiment, as Rumford did, . . . cannot be lightly passed over. Hardly anything more powerful against the materiality of heat has been since adduced; hardly anything more conclusive in the way of establishing that heat is, what Rumford considered it to be, Motion.'

"On the mechanical theory of heat, as a foundation, has been erected the grandest generalization of physical science, the Conservation of Energy. The results of observation and calculation agree, whenever a comparison is practicable, if the calculation is made upon the assumption that the totality of energy in a system, potential as well as dynamical, is as unchangeable as the totality of matter. This sweeping generalization includes and interprets Grove's experimental demonstration of the correlation and convertibility of the different forms of energy, known under the familiar names of gravity, elasticity, light, heat, electricity, magnetism, and chemical affinities. The conversion of heat (which is supplied to an indefinite amount by the consumption of the forests and the coal-beds) into ordinary mechanical energy or work, is of the highest significance to the advancing civilization of the race; but heat cannot be transformed into work without the transformation of a larger amount of heat of high temperature into heat of low temperature. This passage of heat from hot to cold bodies, without doing work, reinforced by the conduction and radiation of heat, creates the tendency to what is now called the dissipation of heat. This is what

the writer in the *London Spectator* meant when he called heat the communist of the universe, the final consummation of this dissipation being a second chaos. Sir William Thomson has computed that the sun has lost through its radiations hundreds of times as much mechanical energy as is represented by the motions of all the planets. The energy thus dispensed to the solar system, and from it to remoter space, 'is dissipated, always more and more widely, through endless space, and never has been, and probably never can be, restored to the sun without acts as much beyond the scope of human intelligence as a creation or annihilation of energy, or of matter itself, would be.' Therefore, unless the sun has foreign supplies, in the fall of meteors or otherwise, where its drafts will be honored, its days are numbered.

"What I have attempted to state in language as little technical as possible is tersely expressed by Clausius in two short sentences: 'The energy of the world is constant.' 'The entropy of the world (that is, the energy not available for work) tends constantly towards a maximum.'"

"Professor J. Willard Gibbs takes his departure from these two propositions when he enters upon his investigation on the 'Equilibrium of Heterogeneous Substances.' Any adequate theoretical treatment of this complex subject must be, necessarily, highly mathematical, and intelligible only to those familiar with the analytical theory of heat. To assist the imagination, Professor Gibbs has devised various geometrical constructions; especially one, of a curved surface, in which each point represents, through its three rectangular coördinates, the volume, energy, and entropy of a body in one of its momentary conditions. The late Professor J. C. Maxwell (whose early death is ever a fresh grief to science) devoted thirteen pages of the fourth edition of his 'Treatise on Heat' to the elucidation and application of these constructions; and it is understood that he embodied in a visible model the equations in which Professor Gibbs expressed his strange surface. In a lecture delivered before the Chemical Society of London, Professor Maxwell gave publicly the endorsement of his great name to the merits of these researches which we are now met to honor. He says: 'I must not, however, omit to mention a most important American contribution to this part of thermodynamics by Professor Willard Gibbs, of Yale College, U. S., who has given us a remarkably simple and thoroughly satisfactory method of representing the relations of the different states of matter, by means of a model. By means of this model, problems which had long resisted the efforts of myself and others may be solved at once.'

"It is now my pleasant duty to present, in the name of the Academy and with their approving voice, the gold and silver medals to the Recording Secretary, Professor Trowbridge, who has been commissioned by Professor Gibbs to represent him on this occasion. I cannot but think that if Count Rumford were living, he would regard with peculiar pleasure this award. For the researches of Professor Gibbs are the consummate flower and fruit of seeds planted by Rumford himself, though in an unpromising soil, almost a century ago. In transmitting these medals to Professor Gibbs, by which the Academy desires to honor and to crown his profound scientific work, be pleased to assure him of my warm congratulations and of the felicitations of all the Fellows of the Academy, here assembled to administer Count Rumford's Trust."

In reply to the President's address, the Recording Secretary then read the following letter from Professor Gibbs: —

"TO THE AMERICAN ACADEMY OF ARTS AND SCIENCES: —

"*Gentlemen*, — Regretting that I am unable to be present at the meeting to which I have been invited by your President, I desire to express my appreciation of the very distinguished honor which you have thought fit to confer upon me. This mark of approbation of my treatment of questions in thermo-dynamics is the more gratifying, as the value of theoretical investigation is more difficult to estimate than the results obtained in other fields of labor. One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity. The success of the investigation in this respect is a matter which he who makes them may be least able to form a correct judgment. It is, therefore, an especial satisfaction to find one's methods approved by competent judges.

"The leading idea which I followed in my paper on the Equilibrium of Heterogeneous Substances was to develop the rôles of energy and entropy in the theory of thermo-dynamic equilibrium. By means of these quantities the general condition of equilibrium is easily expressed, and by applying this to various cases we are led at once to the special conditions which characterize them. We thus obtain the consequences resulting from the fundamental principles of thermo-dynamics (which are implied in the definitions of energy and entropy) by a process which seems more simple, and which lends itself more readily to the solution of problems, than the usual method, in which the several parts

of a cyclic operation are explicitly and separately considered. Although my results were in a large measure such as had previously been demonstrated by other methods, yet, as I readily obtained those which were to me before unknown, or but vaguely known, I was confirmed in my belief in the suitableness of the method adopted.

"A distinguished German physicist has said, — if my memory serves me aright, — that it is the office of theoretical investigation to give the form in which the results of experiment may be expressed. In the present case we are led to certain functions which play the principal part in determining the behavior of matter in respect to chemical equilibrium. The forms of these functions, however, remain to be determined by experiment, and here we meet the greatest difficulties, and find an inexhaustible field of labor. In most cases, probably, we must content ourselves at first with finding out what we can about these functions without expecting to arrive immediately at complete expressions of them. Only in the simplest case, that of gases, have I been able to write the equation expressing such a function for a body of variable composition, and here the equation only holds with a degree of approximation corresponding to the approach of the gas to the state which we call perfect.

"Gratefully acknowledging the very favorable view which you have taken of my efforts, I remain, gentlemen, very truly yours,

"J. WILLARD GIBBS.

"NEW HAVEN, Jan. 10, 1881."

The following papers were presented: —

"Discovery of Palæolithic Flint Implements in Upper Egypt." By Henry W. Haynes.

"On Telegraphing across Bodies of Water without the Use of a Cable." By John Trowbridge.

"Anticipation of the Lissajous Curves." By Joseph Lovering.

Dr. William Everett presented the following suggested emendation of Shakespeare: —

"HAMLET, Act I. Sc. 4.

" 'The dram of eale  
Doth all the noble substance of a doubt  
To his own scandal.' "

"Every reader of Shakespeare has been puzzled by these words; and every critical student of him knows that they are the *cruz* of



textual criticism. Many excellent editors, like R. G. White, leave them as above. The fact that the folio omits them, and that we have only quarto authority for their existence, does not help us. Still, something has been done, and one or two points may be accepted as proved; and as such they will be assumed here. 1st. The word *eale* is a strange misprint for some word denoting *harm*; as, *bad*, *bale*, *base*, *evil*, or *ill*. 2d. *Of* contains the elements of *oft*. 3d. The words *a doubt* contain a verb to which *doth* is the auxiliary; and *dram* and *substance* supply the subject and object.

"Hence have resulted a variety of conjectural emendations, all more or less plausible as far as their resemblance in letters goes. The general sense of them is the same, and is that of the following, which I give, not as a *possible reading*, but as a kind of paraphrase of what all emendations convey:—

The dram of *wrong*  
Doth all the noble substance *oft infect*  
To his own scandal;

making *dram* the subject and *substance* the object.

"Now it seems to me that all emendations in this direction miss the fact that it is *the noble substance* that suffers scandal. The *dram of corruption* can get no *scandal*; yet in this thought it is the agent—the subject—that does something to its *own scandal*; for *own* cannot be used of the object or thing acted on. This is purely a grammatical necessity independently of the sense, and will be seen by putting *X* and *Y* for *the dram* and *the substance*.

"Therefore, to give *own* its proper force, it must refer to the subject of *doth* [*Y*], that is, *the noble substance* is the subject, *the dram of* [*X*] must be the object, and the missing verb must be one properly expressing what *a noble nature* does to *a small element of corruption*.

"I do not pretend to decide on the proper reading for *eale*. I am inclined to prefer *ill*; but as far as the verb goes, I feel little doubt.

"Read,

This dram of *ill* (?)  
Doth all the noble substance *oft adopt*  
To his own scandal.

"If *adopt* were read off to some Holofernes of the printing-office who refused to say '*dout*, fine, when he should pronounce *doubt*,' we have the beginnings of the *textus receptus* at once."



The following paper was presented by title:—

“On the Use of the Electric Telegraph during Total Solar Eclipses.” By D. P. Todd.

On the motion of Professor Cooke, it was

*Voted*, To adjourn this meeting to the second Wednesday in February.

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Seven hundred and thirty-eighth Meeting.

February 9, 1881. — ADJOURNED STATED MEETING.

The PRESIDENT in the chair.

Professor Lovering read a report from the Rumford Committee. In accordance with the recommendation of the committee, it was

*Voted*, To appropriate four hundred dollars (\$400) for the purchase of books on light and heat, at the discretion of Mr. Scudder; also,

*Voted*, That three hundred dollars (\$300) be appropriated to Professor S. P. Langley, for experiments on the distribution of heat in the diffraction spectrum.

The following papers were presented:—

“Observations on the Senses of Sight and Touch.” By Henry P. Bowditch.

“Thermo-dynamic Basis of the Kinetic Theory of Gases.” By N. D. C. Hodges.

“Strength and Stiffness of small Spruce Beams.” By F. E. Kidder; presented by Professor Cross.

“Variable Stars of Short Period.” By Edward C. Pickering.

“On the Propagation of Magnetic Waves in Soft Iron.” By Harold Whiting; presented by Professor Trowbridge.

“Observations on the Zodiacal Light.” By Arthur Searle.

“Curcumine.” By C. Loring Jackson.

Charles Edouard Brown-Séquard, of Paris, was elected a Foreign Honorary Member in Class II., Section 4.

## Seven hundred and thirty-ninth Meeting.

March 9, 1881. — STATED MEETING.

The PRESIDENT in the chair.

The President announced the death of Mr. George B. Emerson, the Senior Fellow of the Academy.

The following papers were presented by title : —

“General Properties of certain Partial Differential Equations similar to those of Hydrodynamics.” By Thomas Craig.

“Observations on Jupiter.” By Leopold Trouvelot.

Professor Cooke presented a bound volume of chemical contributions from the laboratory of Harvard College.

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Seven hundred and fortieth Meeting.

April 13, 1881. — MONTHLY MEETING.

The PRESIDENT in the chair.

The President called attention to the copies of the first part of Volume XVI. of the Proceedings on the Table, which were ready for distribution.

The following papers were presented : —

“On large Telescopes.” By E. C. Pickering.

“An Illustration of the Lines of Weakness in Cylinders.” By Robert H. Richards.

“On the Possible Causes of some Phenomena described under the General Name of Zodiacal Light.” By Arthur Searle.

“Studies in Metrology.” First article. By William A. Rogers.

The following papers were presented by title : —

“Photometric Measurements made at the Harvard College Observatory of the Variable Stars  $\beta$  Persei and DM. 81°25.” By Edward C. Pickering.

“On Osmyl Ditetramine.” By Wolcott Gibbs.

Seven hundred and forty-first Meeting.

May 11, 1881. — MONTHLY MEETING.

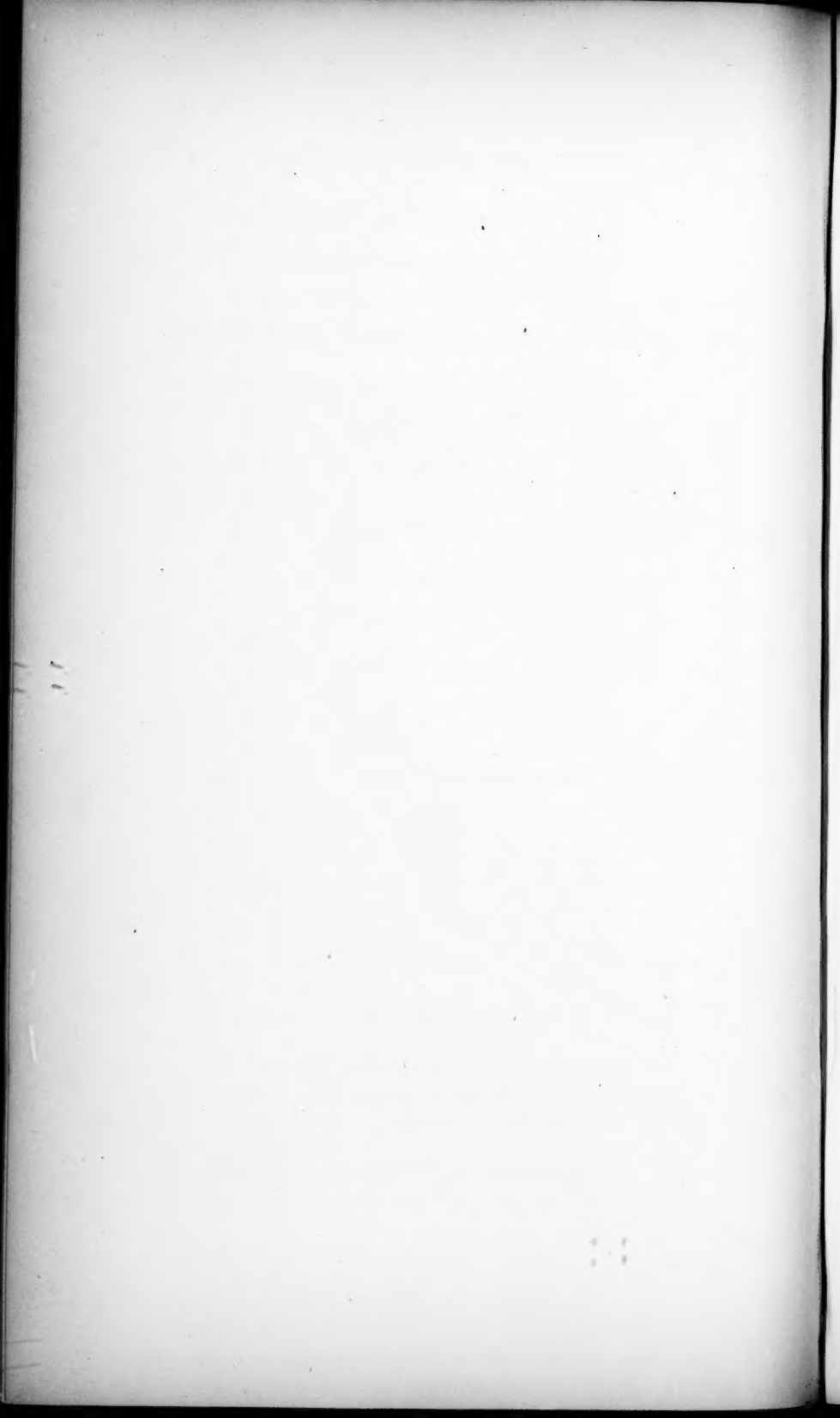
The PRESIDENT in the chair.

Mr. Arthur Searle presented a communication on the zodiacal light.

Professor Josiah P. Cooke made some remarks on Prout's Law, and presented the following papers by students in the Chemical Laboratory of Harvard College:—

“On the Atomic Weight of Copper.” By G. M. Hyams.

“On the Atomic Weight of Cadmium.” By O. W. Huntington.



## REPORT OF THE COUNCIL.

MAY 24, 1881.

SINCE the last report, May 25, 1880, the Academy has received notice of the death of thirteen members, as follows: six Resident Fellows, George B. Emerson, John C. Gray, Charles T. Jackson, Stephen P. Ruggles, L. F. Pourtalès, and Benjamin Peirce; three Associate Fellows, J. L. Diman, S. S. Haldeman, and James C. Watson; four foreign Honorary Members, Thomas Carlyle, Michel Chasles, W. H. Miller, and C. A. F. Peters.

### RESIDENT FELLOWS.

#### GEORGE B. EMERSON.

GEORGE B. EMERSON, who died March 4, 1881, was born in Wells, Me. (then a part of Massachusetts), Sept. 12, 1797. Dr. Emerson, his father, was a physician, with much cultivation outside of his profession. At his house the children came in contact with a refined and intellectual society. They went to school in the winter, and were engaged upon their father's farm in the summer, where their powers of observation were developed. The subject of this notice was familiar, at an early age, with the trees, plants, and shrubs in the vicinity of his home, and read with avidity everything upon botany that was within his reach. He knew something of Latin and Greek before he entered Dummer Academy, at Byfield, where he prepared for college. In Harvard College, which he entered in 1813, he was studious to a fault, sacrificing his sleep, and finally his health, to his desire for improvement. After graduating in 1817, he taught successfully a private school in Lancaster, Mass., having had some experience in teaching country schools in his college vacations. In 1819 he came to Cambridge, and was tutor in mathematics in the College. When the English Classical School was established in Boston, Mr. Emerson was

selected as the first principal, and gave complete satisfaction. In 1823 he organized his private school for ladies, which helped to mould a whole generation of the young, and was the great work of his life. It was not only what he taught, but what he was, that lent weight to his teaching. He gave up his school when the time came for seeking recreation in Europe. He often expressed his regret that he did not resume it, on his return. But his high office, as an educator, was not confined to his school, or to Boston, but was as broad as New England; and that office he never resigned. It is idle to speculate as to what his career would have been, if his mother's wishes had not prevailed over a fancy of his boyhood which looked to West Point rather than to Harvard. If, however, he had carried out the maturer purpose of his heart, which was to enter the Christian ministry, though his success there was assured, he would have left vacant a place not easily filled by any other man.

Next to Mr. Emerson's services in education, — to which his life was early consecrated, — his services to natural sciences, especially to their popularization, and their proper teaching, are most worthy of remembrance in this Academy. At one time the course of his life might have wholly turned in this direction, when, as he himself informed us, the new Fisher Professorship of Natural History and the direction of the Botanic Garden, having been declined by Dr. Francis Boott, were offered to him. The offer was a tempting one, and very congenial to his tastes; but he had successfully entered upon his chosen career, had proved his powers in it, and he preferred not to break away from it. No doubt he felt that it was too late for him to do justice to himself and to the cause of science in this vocation; for, although natural history had not yet asserted itself at Cambridge, and hardly elsewhere, he in some degree foresaw its rising importance. All natural science was to deal with deeper and larger questions, by new methods and exacter researches, and its votaries needed long and special training. To the advance that has been made within the last forty years and more, his helping hand and his weighty influence have largely contributed. He was one of the originators of the Boston Society of Natural History, and he was its second President. He was, in the time of Edward Everett's governorship, one of the projectors of the Geological Survey of the Commonwealth, and he bore a leading part in settling its plan and in perfecting its organization. Assigning to the late Professor Dewey — then of Williams College — the report upon the herbaceous vegetation, he himself drew up the account of the Trees and Shrubs of the State in a volume which, next

to the remarkable one of Dr. Harris, is counted as among the best fruits of that survey. The two classics of New England botany are Dr. Bigelow's well-known *Flora* and Mr. Emerson's treatise on the *Trees and Shrubs of Massachusetts*, — both side-issues from active professional life; both unusually successful in the combination of popular with scientific treatment of their subjects, and in the extent of their influence in this community, as also in the appreciation accorded to them by scientific men.

In his later years Mr. Emerson re-edited his *Report*, illustrated it fully, and at much personal cost, by excellent plates in chromo-lithography, from designs by Mr. Isaac Sprague (who had furnished the few outline plates of the original edition), and published it in two large octavo volumes, — volumes which are thought worthy to stand by the side of those of Michaux.

It should here be recorded, moreover, that it was under Mr. Emerson's recommendation and influence that the late Mr. James Arnold made the bequest upon which the Arnold Arboretum is founded.

#### HON. JOHN CHIPMAN GRAY, LL.D.

THE HON. JOHN CHIPMAN GRAY, LL.D., died in Boston on the 3d of March, 1881, in his eighty-eighth year, having been born in Salem, Mass., Dec. 26, 1793. He was graduated at Harvard University, in 1811, in the class with Edward Everett, of whom he was the chum at Cambridge, and a life-long friend. He studied law, and was admitted to the bar; but, inheriting an ample fortune from his father, he did not pursue the practice of his profession. He was early engaged in public life, and, for a long term of years, did excellent service to the State, as a member of both branches of the Legislature, successively, and as a member of the Executive Council of the Commonwealth. He was deeply interested in agricultural pursuits, and was for many years President of the old Massachusetts Society for the Promotion of Agriculture. Mr. Gray was a great reader, and an able and instructive writer, contributing many articles to magazines and journals, and leaving a volume of valuable essays to bear witness to his literary accomplishments.



## CHARLES THOMAS JACKSON.

CHARLES THOMAS JACKSON was born at Plymouth, Mass., June 21, 1805. He studied medicine at the Medical School of Harvard University, and in 1829 received the degree of Doctor of Medicine. Soon after he visited Europe to complete his studies, and at Paris formed the acquaintance of men eminent in science, and, among others, of the celebrated geologist, Elie de Beaumont, who exerted a marked influence on his subsequent career. Before completing his course at the Medical School, he had already manifested a strong interest in geology, mineralogy, and chemistry; and, in company with his friend, Mr. Francis Alger, had explored a considerable portion of Nova Scotia. The special interests and aptitudes thus manifested drew him away from the practice of medicine, and led him to devote himself to scientific study, and to the solution of problems in practical science. He was one of the first in this country to establish a chemical laboratory for students, as well as for commercial work. Several of Doctor Jackson's early students became subsequently highly distinguished; and the numerous practical problems which were successfully solved in his laboratory gave to him a wide reputation as an expert in geology and chemistry.

Doctor Jackson was elected a Fellow of this Academy in 1837. He had previously published in our *Memoirs* (New Series, Vol. I.), in connection with Mr. Francis Alger, an extended paper upon the "Mineralogy and Geology of Nova Scotia;" and he subsequently contributed to our "Proceedings," "Remarks upon a large Vein of Phosphate of Lime, found at Hurdstown, New Jersey;" "Analyses of Water;" "Analysis of Bornite for Georgia;" "Results of an Examination of the Frozen Well at Brandon, Vermont;" "Analysis of Meteoric Iron from Dacotah."

Of the Natural History Society of Boston, Doctor Jackson was one of the earliest and most active members. He held several of its offices, and was for many years one of its Vice-Presidents. To this society he made very frequent communications; and in its "Proceedings," from their first publication in 1841 until he became enfeebled by illness, there may be found constantly recurring notices of the part taken by him in the discussions at its meetings. His contributions to the "American Journal of Science" were likewise numerous; and among the papers which occur in one or the other of these publications may be mentioned, Analyses of the Mineral Waters of the

Azores; Remarks on the Geology of Maine; Chemical Analysis of Meteoric Iron from Claiborne, Alabama; Bitumenization of Peat, and its Conversion into Coal; An Account of the Catlinite, or Indian Pipe Quarry; The Lava of the Volcano of Kilauea in Hawaii, and its Chemical Composition; Remarks upon Drift, and upon the Organic Matters of Soils; The Concrinite, Nepheline, and Zircon of Litchfield, Maine; The Ores of Lake Superior; The Discovery of Tellurium in Virginia; Analyses and Description of the Vermiculite of Millbury, Mass.; The Lake Superior Copper Region; The Asphaltic Coal of New Brunswick; The Discovery of Fossil Fish in the Coal Formation of New Brunswick.

In the volume of the "Proceedings of the Association of American Geologists and Naturalists" may be found a description by Doctor Jackson of the veins of tin ore of Jackson, New Hampshire, and remarks upon the zinc, copper, and lead ores of the same State. In the subsequent volumes of the American Association for the Advancement of Science he published: Observations on a Mirage seen at Lake Superior; Remarks on the Geology, Mineralogy, and Mines of Keneewaw Point; On Ancient Pot-holes in Rocks; Description and Analyses of Allanite from Franklin, New Jersey; Description of Bismuthic Tellurium from Virginia; Artificial Minerals from an Iron Furnace of Pennsylvania.

Doctor Jackson published also in the "American Journal of Agriculture," in the "Boston Medical and Surgical Journal," and in the "Comptes Rendus of Paris." We are unable to make the catalogue complete; but the titles we have quoted are sufficient to give an idea of the great extent and variety of the work which is shown even by his shorter papers. But all this was subordinate to the extensive and important Geological Surveys, on which he was early employed, and of which he was one of the pioneers in this country.

The first report of our late associate on the "Geology of the State of Maine" appeared in 1837, and was followed by the second in 1838, and the third in 1839. Additional reports upon the "Public Lands of Maine" were likewise published in the two former years. In 1840 his final report on the "Geology of Rhode Island" was issued. In 1841 his first report on the "Geology of New Hampshire" was printed, followed by a second report in 1842; and his final report on the geology of that State was published in a quarto volume in 1844. Lastly, in 1849, Doctor Jackson's report on the "Mineral Lands of the United States in Michigan" appeared at Washington in an octavo volume with maps. It will be noticed that the geological work, whose

results are embodied in these reports, was all finished before 1849; and it is obvious, therefore, that it ought not to be judged by the standard of a more advanced science. It was a most important work for the time, and greatly helped to develop the mineral resources of the country.

This necessarily imperfect account of Doctor Jackson's scientific work forms a most worthy record: and we would that our notice of his life might end here; for the unfortunate controversy which overshadowed his later years brought only sorrow and disappointment to him, and diverted attention from the valuable services he had rendered to industrial science. The discovery of anæsthesia, like the discovery of printing, was too great a gift for any one man to confer on his race. That Doctor Jackson suggested the use of ether for producing insensibility to pain, and that this suggestion was based on previous experience, seems unquestionable. But it was not a suggestion, however fruitful; not an unimproved experience, however important; not a rash experiment, though called courageous when successful: but the careful and cautious investigation of the conditions of success and the limits of safety, that constituted the great gift for which mankind should be grateful. The monument erected on the Public Garden in Boston, in honor of the discovery of anæsthesia, by blazoning no man's name, implicitly records the verdict in which most thinking men acquiesce; and the one great lesson which the "Ether Controversy" should teach is that for such great gifts, not to man, but to God, belongs all the glory.

It is, however, a painful fact that Doctor Jackson honestly believed himself entitled to the whole honor of the discovery of anæsthesia, and that his later years were embittered by what he regarded as the injustice and ingratitude of his contemporaries. His unsuccessful efforts to obtain a recognition of his claims; the engrossment of mind, anxiety, suffering, and disappointment, occasioned by the controversy, — led finally to insanity, which separated him from his family and friends several years ago; and when, on the 29th of August last, the news came that the troubled spirit was at length at rest, the survivors of those friends whom his bright intellect had drawn around him in his early manhood felt that a long night of mourning had passed.

## STEPHEN PRESTON RUGGLES.

STEPHEN PRESTON RUGGLES was born in Windsor, Vt., July 4, 1808. He was a descendant of Thomas Ruggles, who emigrated from Nazing, Essex, England, to Roxbury, Mass., in 1637. As a school-boy he showed his predilection for mechanism by inventing and building several little machines, which arrested the attention of the mechanics of the neighborhood; one of these was a rotary pump, which, though rudely built, worked with great efficiency.

Apprenticed at the age of fifteen to a printer, he soon began to devise means of improving the printing-press. His first successful attempt was the invention of a self-acting roller to ink the types of a hand-press; although the apparatus had been constructed in the cheapest possible manner, it worked well and silenced the jeers and laughter of those who had opposed the plan.

About this time stereotype plates began to be used. Although the process of stereotyping was a profound secret, and he was ignorant even of the existence of such a material as plaster of Paris, of which the moulds are made, yet he succeeded in producing casts of wood engravings, and of type, of a very satisfactory character.

In 1826 he came to Boston an entire stranger, with less than three dollars in his pocket. He, however, found employment, and soon after built with his own hands the first cylinder power-press ever constructed in this country.

He next invented a double-frisket bed and platen press, and built a complete working model, which was exhibited during the summer of 1827. This same year he built the first belt or band saw ever used. He, however, neglected to take out a patent, and it was subsequently patented by others, and is now in successful operation in all parts of the country.

From 1827 to 1832 he invented a new ruling-machine for the use of engravers, and the first card or job press that was, probably, ever constructed; he succeeded by this press in printing upon dry, polished, or calendered paper without wetting it, and without making any impression in the paper.

In 1833 Mr. Ruggles took charge of the printing at the Perkins' Institution for the Blind. The following extracts from the "American Cabinet and Boston Athenæum" of Dec. 1, 1849, give an idea of the difficulties encountered in his new task.

The books for the blind, as they were then made in Europe, were

bulky and unwieldy, as well as costly; with quick perception he very soon ascertained that he could produce a type of less size and less height of face, which the blind could read as well, if not better, than the old-fashioned kind. He accordingly altered the size, the height and bevel of the face of the type repeatedly, each time taking impressions and practising reading with the blind pupils till he informed himself accurately what they could read best. By these experiments he made himself acquainted with the important fact, that, if the type were comparatively small and the face but slightly raised, they could be read with ease and rapidity, provided the raised impression on the paper was hard and sharp.

Having prepared the type, he now commenced printing, and after many trials and experiments with the strongest printing-presses in use, and after breaking two of them without succeeding in obtaining such an impression as he required, he was obliged to invent and build a more powerful press of an entirely new construction. This new press he so contrived that it could be worked by the blind; and, while it gave a pressure of three hundred tons at each impression, would at the same time throw off work at the rate of eighteen sheets per minute, thus working about as fast as the ordinary newspaper power-presses.

After succeeding in the construction, both of his type and press, a new and unexpected difficulty presented itself.

There was no paper to be found properly adapted for the purpose of this kind of printing or embossing. That which was hard enough would break through, and be rough, when embossed or printed; and that which was flexible enough not to crack or break through would flatten down when pressed upon by the fingers of the reader. However, after many experiments on the manufacture of paper with gums, resins, and gelatine, he produced a paper stiff and hard, like parchment, that would receive a sharp and distinct impression, that would stand firm and unyielding when pressed by the fingers, and that would not break or crack under the pressure of the press.

After perfecting the new method of printing books, Mr. Ruggles next invented a new method of making *maps* for the blind, which proved eminently successful. This he accomplished by a raised character similar to his type, but arranged with such combinations that at a trifling expense he could produce a succession of maps of any size and of any country. Maps made in this manner were never before known, and the Perkins Institution in Boston immediately issued an "Atlas of the United States, and a General Atlas."

We cannot in this brief notice call attention to all of Mr. Ruggles's

valuable improvements for facilitating the education of the blind, but much of the school apparatus now in use is his invention.

In 1838 he resigned his position at the Perkins Institution, and from that time devoted himself to his inventions. These included improved forms of printing, stamping, and punching presses; machines for cutting paper, cards, and sheet metal, for planing stereotype plates, and for laying out the teeth of gear wheels; improvements in hand-stamps, couplings for shafts, a new form of steam generator, a registering dynamometer, a gas regulator, etc. For these inventions he has received no less than nine medals of bronze, silver, and gold from different corporations in recognition of his extraordinary mechanical achievements.

Mr. Ruggles earnestly advocated the establishment by the state, city, or by an endowed corporation, of what he called "Developing Schools and School Shops," in which a boy after leaving the common school should be taught that trade, art, or calling for which he is best fitted by nature; the object of the developing school being to ascertain by actual experiment, in a series of miniature workshops, the occupation best adapted to the capacity of the pupil.

Mr. Ruggles also advocated the establishment of a "Museum of Mechanism" for the use of students and inventors, which should contain a complete collection of kinematic models, as well as types of important machines. These two projects occupied him exclusively for the last years of his life up to the time of his death, which took place at Keene, N. H., May 28, 1880.

Mr. Ruggles was always greatly interested in technical education, and was ever ready to aid in perfecting the apparatus for instruction in applied science.

#### LOUIS F. DE POURTALES.

LOUIS F. DE POURTALES was born in Neuchâtel on the 4th of March, 1824, and died at Beverly Farms, on the 17th of July, 1880, in the fifty-seventh year of his age, sinking after a severe illness under an internal malady. The blow fell the more heavily upon his family and friends and upon his scientific colleagues, because his fine constitution, combined with a manly vigor of body and mind, had seemed to defy disease and to promise years of activity.

Educated as an engineer, he showed from boyhood a predilection for natural history. He was a favorite student of Professor Agassiz, and when only a lad of seventeen had shared his labors on the glacier



of the Aar, being one of the party of Alpine explorers who, in 1810, made their home under the famous boulder known as the *Hotel des Neuchâtelois*. When his friend and teacher came to America in 1847, he accompanied him, and remained for some time with the little band of naturalists who, first at East Boston and subsequently at Cambridge, shared his labors. In 1848 Pourtalès entered the United States Coast Survey, where his ability and indefatigable industry were at once recognized, and he remained attached to that branch of our public service for many years.

In 1851 he was engaged as assistant on the triangulation of the Florida Reef. While there he collected a number of Gephyreans and Holothurians which he described in the *Proceedings of the American Association for the Advancement of Science*, together with a number of species observed by him while living at East Boston and assisting Professor Agassiz in the preparation of his text-book on Zoölogy, afterwards published by him in conjunction with Dr. Gould. For this text-book Pourtalès prepared the greater number of the drawings. These descriptions and those of Dr. Gould and Dr. Stimpson formed for a long time the only literature of the large number of Annelids and Holothurians, now so well known through the investigations of the Fish Commission along the Atlantic coast of the United States.

Thus prepared, Pourtalès became deeply interested in everything relating to the study of the bed of the ocean. Thanks to the enlightened support of the then Superintendent of the Coast Survey, Professor Bache, and of his successors, Professor Peirce and Captain Patterson, he was enabled to devote his talents and industry to the comparatively new field of "Thalassography" and the biological investigations related to it. So interesting and valuable were the results obtained, not only as an aid to navigation, but in their wider bearing on the history of the Gulf Stream and on the distribution of animal life at great depths, that in 1866 he was sent out by Professor Peirce, then Superintendent of the Coast Survey, to continue these investigations on a larger scale. The large collections of samples of sea-bottom accumulated by the different hydrographic expeditions of the United States Coast Survey were carefully examined by him; and the results, accompanied by a chart of the sea-bottom on the east coast of the United States, were published in Petermann's "*Mittheilungen*," in advance of their appearance in the Coast Survey Reports.

From 1854 until his resignation as Assistant in the United States Coast Survey, Mr. Pourtalès had charge of the field and office work



of the Tidal Division. His reports to the Superintendent of the United States Coast Survey, incorporated in the annual Reports, short as they are, show the amount and value of his work. In addition to this tidal work, he was also at times assigned to special duty, as, for instance, at the magnetic station at Eastport. Previously to taking charge of the Tidal Division, he had been acting under the more direct supervision of the Superintendent of the Coast Survey, either in connection with the tidal work or the calculation of longitudes.

While in Florida his attention was drawn to the habits of the Foraminifera, then little known, and his first papers on this subject were read at the meeting of the American Association for the Advancement of Science for 1850. They at once attracted attention, and after the death of Professor Baily of West Point the larger series of samples from the sea-bottoms, collected by the officers of the Coast Survey, were submitted to him for examination. At that time the opinion of Forbes, that the depths of the sea were absolutely barren of life, was still generally accepted. Sharing this view with other naturalists, Pourtales was nevertheless led to reconsider it in connection with his observations on his Foraminifera, many of which had been brought up from depths far below that considered by Forbes to be the limit of life. Did they belong there, or was their natural habitat, like that of others of their kind,\* nearer the surface; and had they simply dropped to the bottom after death, or been gradually washed down from the reefs by the current? This question is discussed with much keenness of observation in his report on the Foraminifera collected by Craven and Maffitt. He inclined to believe that they actually lived where they were found, because the greater number of individuals in these specimens are brought up in perfect condition, notwithstanding the extreme delicacy of their shells. The faint pink color of the Globigerinæ, for instance, could scarcely be preserved had the specimens been transported from a distance, and the best argument in favor of their deeper habitat is found in the fact that the same species are found uninjured (and at great depths) as far north as New Jersey. It is, however, still most perplexing that the same species are also found living near Cuba and elsewhere in the West Indies under very different conditions of light and temperature.

He clearly saw that our ideas of the bathymetrical distribution of the higher Invertebrates were to be greatly modified; for he says in one

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\* Mr. Pourtales, in 1867, observed a species of *Globigerina* floating on the surface off Havana.

part of the report: "There are some delicate shells of mollusks from depths beyond five hundred fathoms where they were certainly living." He also called attention to the existence of green sand as one of the characteristic deep-sea formations of the present day. "A mixture in about equal proportions of Globigerinæ and black sand—probably green sand." In concluding he called attention to the importance for geologists of a knowledge of the habitat and distribution of Foraminifera, on account of their large share in the formation of rocks, at least in the Cretaceous and Tertiary periods.

While examining the samples of bottom collected by Commander Sands, he made the discovery that many specimens of *Orbulina* contained a young *Globigerina*, more or less developed, so that the two genera must be considered as probably two stages of alternate generation. He was also able, in some of the specimens collected by Commander Sands, to trace the successive changes of the Foraminifera into green sand, from the most fresh-looking Foraminifera of various species until all trace of their origin was apparently lost.

In 1858 he gave a general report of his work on the Foraminifera of the bottoms collected by the various Gulf Stream expeditions up to that time. This was by no means the close of his studies in this direction, for he continued as a part of his duties of Assistant on the Coast Survey to have charge of the collection of bottom deposits. The general results of his studies he published in Petermann's "Geographische Mittheilungen" for 1871, with a map showing the geographical and bathymetrical distribution of the different bottoms on the east coast of the Atlantic. Fitted as he was both by taste and early training for zoölogical studies, it was natural that the Coast Survey should look to him for an expansion of its biological work, and in 1867 he was assigned to the Coast Survey steamer *Corwin* in order to make such biological collections as would tend to elucidate the fauna of the bottom of the Gulf Stream between the Florida Keys and Cuba. The breaking out of yellow-fever on board the steamer after a few casts had been taken put a stop to all further work for that season. But early in 1868 the campaign was opened again with such success, Acting Master Platt, U. S. N., commanding the Coast Survey steamer *Corwin*, that Mr. Pourtales induced Professor Agassiz, who had become greatly interested in the extraordinary results of the second expedition, to join him in the Bibb for the third cruise in 1869. The second expedition, from the brilliant results obtained, may be said to have awakened general interest in the subject of the bathymetrical distribution of animal life. The discovery alone of the great range in

depth of Rhizocrinus from the Straits of Florida to the Loffoden Islands opened a field of investigation, dimly foreshadowed, it is true, by the earlier dredgings of the older and younger Sars, and the wider bearing of which Lovén had anticipated in a paper read before a meeting of the Scandinavian naturalists as early as 1863.

In the Coast Survey Reports for 1867 and 1868 are to be found Pourtalès's first reports on the fauna of the Gulf Stream in the Straits of Florida. These reports were published with greater biological detail in the first volume of the *Bulletins of the Museum of Comparative Zoölogy* for 1867 and 1868.

The large and valuable collections made by Mr. Pourtalès in the Gulf Stream, as well as those made under his direction on board the *Hassler*, were deposited at the Museum of Comparative Zoölogy, Cambridge, and thence distributed as rapidly as possible to be worked up by specialists throughout the scientific world. To these were afterward added the results of the three Blake expeditions, which were indeed the natural continuation of the work initiated by Pourtalès. The collections thus sown broadcast have already borne a rich harvest in special reports upon Echinoderms, Corals, Crinoids, Foraminifera, Sponges, Annelids, Hydroids, Bryozoa, Mollusks, and Crustacea, prepared by the most eminent investigators of America and Europe, and published principally in the *Bulletins of the Museum*. They form a part of that series of international monographs to which Sir Wyville Thomson, following the liberal policy adopted and advised by the Director of the Museum, is making such generous contributions through the collections of the *Challenger*.

An examination of the characteristic deep-sea Echinoderms, Sponges, and Corals showed at once the ancient characters of the types; while the similarity of the genera of Echini to those of the chalk, the discovery of representatives of the Infusteridæ (*Pourtalesia*),\* of *Salenia*, of *Hemipedina*, *Conoclypus*, and others, led the way to the theories of Thomson regarding the great antiquity of these forms and to the modern theories as to the formation of the chalk. The old view of Guyot and of Dana upon the great antiquity of continents and of oceanic basins received also a strong support from the data obtained in Mr. Pourtalès's dredgings. The specimens of bottom showed conclusively that we had not had, in former geological times,

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\* This genus is the representative of the most interesting family of Echini brought to light by deep-sea dredging: it was named in honor of Pourtalès in 1869.

any deposits strictly corresponding to those now forming at the bottom of the ocean in great depths.

Mr. Pourtalès was indeed the pioneer of deep-sea dredging in America, and he lived long enough to see that these earlier expeditions had paved the way not only for similar English, French, and Scandinavian researches, but had led in this country to the Hassler and finally to the Blake expeditions under the auspices of the Hon. Carlile Patterson, the present Superintendent of our Coast Survey. On the Hassler Expedition, from Massachusetts Bay through the Straits of Magellan to California, he had entire charge of the dredging operations. Owing to circumstances beyond his control, the deep-sea explorations of that expedition were not as successful as he anticipated.

At the death of his father, Mr. Pourtalès was left in an independent position, which allowed him to devote himself more completely than ever to his zoological studies. He resigned his official connection with the Coast Survey, and returned to Cambridge, where he became thenceforth identified with the progress of the Museum of Comparative Zoölogy. To Professor Agassiz his presence there was invaluable. In youth one of his favorite pupils, throughout life his friend and colleague, he now became the support of his failing strength.

Mr. Pourtalès reserved to himself the corals, Halcyonarians, Holothurians, and Crinoids, of the different deep-sea dredging expeditions with which he was connected. A number of his papers on the deep-sea corals of Florida, of the Caribbean Sea, and of the Gulf of Mexico, have appeared in the Museum publications. The Crinoid memoirs published by him relate to a few new species of Comatulæ, and to the interesting genera *Rhizocrinus* and *Holopus*.

At the time of his death Mr. Pourtalès was engaged in the study of the Holothurians and the magnificent collection of Halcyonarians of the Blake. Unfortunately he had not advanced far enough in his preliminary work to make its completion possible; so that the Holothurians of the Blake will now be worked up with those of the Challenger, while the Halcyonarians must be left undetermined for the present, the Antipatharia alone having been finished.

His largest and most important work is his monograph on the deep-sea corals, published as one of the illustrated catalogues of the Museum of Comparative Zoölogy. This was published in 1871, and in it he describes the corals he collected in the years 1867-1869, while on the Coast Survey expeditions to explore the Gulf Stream. As an introduction to the memoir, we find a short *résumé* of the conditions of

the floor of the Gulf Stream between Cuba, the Bahamas, and the Florida Keys, and a map with sections and other details showing the ground covered by the dredgings of Mr. Pourtalès. Throughout the memoir there are scattered most important general remarks on the affinities of the different families, the most interesting of which are those on the Rugosa and the Stylasteridæ. He also wrote for Appleton's Cyclopædia a number of articles on the Atlantic, Indian, and Pacific Oceans, on the Polar Seas, the Galapagos, the Straits of Magellan, Juan Fernandez, and Deep-sea Dredging.

The titles of his memoirs indicate the range of his learning and his untiring industry. His devotion to science was boundless. A model worker, so quiet that his enthusiasm was known only to those who watched his steadfast labor, he toiled on year after year without a thought of self, wholly engrossed in his search after truth. He never entered into a single scientific controversy, nor even asserted or defended his claims to discoveries of his own which had escaped attention. But while modest to a fault, and absolutely careless of his own position, he could rebuke in a peculiarly effective though always courteous manner ignorant pretensions or an assumption of infallibility.

Appointed keeper of the Museum of Comparative Zoölogy after the death of Professor Agassiz, he devoted a large part of his time to the administration of the Museum affairs. Always at his post, he passed from his original investigations to practical details, carrying out plans which he had himself helped to initiate for the growth of the institution. As he had been the devoted friend of Professor Agassiz, he became to his son a wise and affectionate counsellor, without whose help in the last ten years the Museum could not have taken the place it now occupies.

If he did not live to see the realization of his scientific hopes, he lived at least long enough to feel that their fulfilment is only a matter of time. He has followed Wyman and Agassiz, and like them has left his fairest monument in the work he has accomplished and the example he leaves to his successors.

The following are the principal publications of Mr. Pourtalès:—

- 1850.** On the Distribution of Foraminifera on the Coast of New Jersey, as shown by the Off-shore Soundings of the Coast Survey. *Proc. Amer. Assoc. for Adv. of Sc.*, Charleston meeting, 1850.  
On the Order of Succession of Parts in Foraminifera. *Proc. Amer. Assoc. for Adv. of Sc.*, Charleston meeting, 1850. Also *Amer. Journ. of Sc. and Arts*, 2d series, Vol. II. 1851.
- 1851.** On the Holothuridæ of the Atlantic Coast of the United States. *Proc. Amer. Assoc. for Adv. of Sc.*, 1851, p. 8.

- A paper read in 1847 at meeting of Assoc. of Amer. Geol. and Nat. at Boston.
- 1851.** On the Gephyrea of the Atlantic Coast of the United States. Proc. Amer. Assoc. for Adv. of Sc., 1851, p. 39.
- 1853.** Extract from Letters of L. F. Pourtalès, Assistant in the Coast Survey, to the Superintendent upon the Examination of Specimens of Bottom obtained in the Exploration of the Gulf Stream by Lieutenants-Commanding T. A. M. Craven and J. N. Maffitt, U. S. N. Coast Survey Report for 1853, and Proc. Amer. Assoc. for Adv. of Sc., Cleveland meeting, 1853.
- 1854.** Tidal Reports.
- 1858.** Report of Assistant L. F. Pourtalès on the Progress made in the Microscopical Examination of Specimens of Bottom from Deep-Sea Soundings. Coast Survey Report for 1858.
- 1858.** On the Genera *Orbulina* and *Globigerina*. By L. F. Pourtalès. Amer. Journ. of Sc. and Arts, 2d series, Vol. XXXVI. 1858.
- 1867.** Report on the Fauna of the Gulf Stream in the Straits of Florida. By L. F. Pourtalès. Coast Survey Report for 1867.
- Contributions to the Fauna of the Gulf Stream at great Depths. By L. F. Pourtalès, Assistant U. S. Coast Survey. Bull. Mus. Comp. Zool., Vol. I. No. 6. Cambridge, 1867. pp. 18.
- 1868.** Contributions to the Fauna of the Gulf Stream at Great Depths (2d series). By L. F. Pourtalès, Assistant U. S. Coast Survey. Bull. Mus. Comp. Zool., Vol. I. No. 7. Cambridge, 1868. pp. 22.
- 1868.** Report of Assistant L. F. Pourtalès on Dredgings made in the Sea near the Florida Reef. Coast Survey Report for 1868.
- 1869.** The Gulf Stream. Characteristics of the Atlantic Sea-Bottom off the Coast of the United States. By L. F. Pourtalès. Coast Survey Report for 1869.
- 1869.** List of the Crinoids obtained on the Coasts of Florida and Cuba by the U. S. Coast Survey Gulf Stream Expeditions in 1867, 1868, and 1869. By L. F. Pourtalès, Assistant U. S. Coast Survey. Bull. Mus. Comp. Zool., Vol. I. No. 11. Cambridge, 1869. pp. 4.
- 1869.** List of Holothuridæ from the Deep-Sea Dredgings of the United States Coast Survey. By L. F. Pourtalès, Assistant U. S. Coast Survey. Bull. Mus. Comp. Zool., Vol. I. No. 12. Cambridge, 1869. pp. 3.
- 1870.** Der Boden des Golfstromes und der Atlantischen Küste Nord Amerika's. Von L. F. Pourtalès. Petermann's Geograph. Mittheilungen, 1870. Heft XI. pp. 5. 1 map.
- 1871.** Deep-Sea Corals. By L. F. Pourtalès, Assistant U. S. Coast Survey. Illustrated Catalogue of the Mus. Comp. Zool., Vol. II. No. 4. (Memoirs, Vol. II. No. 4.) Cambridge, 1871. pp. 93. Pls. 8.
- 1874.** The Zoological Results of the Hassler Expedition. I. Echini, Crinoids, and Corals. By Alexander Agassiz and L. F. Pourtalès. pp. 54. 15 woodcuts. Pls. 10. II. Ophiuridæ and Astrophytidæ, including those dredged by the late Dr. Stimpson. By Theodore Lyman. Illust. Cat. Mus. Comp. Zool., No. 8. (Memoirs, Vol. IV.) Cambridge, 1874. pp. 34. 4 woodcuts. Pls. 5.
- 1875.** Corals at the Galapagos Islands. By L. F. Pourtalès. Amer. Journ. of Sc. and Arts, 3d series. Vol. X. 1875.



1876. Recent Corals from Tilibiche, Peru. By Alexander Agassiz and L. F. Pourtalès. pp. 4. 1 plate. March, 1876.
1878. Reports on the Dredging Operations U. S. Coast Survey Steamer "Blake." II. Echini. By A. Agassiz.—Corals and Crinoids. By L. F. Pourtalès.—Ophiurans. By T. Lyman.—pp. 58. 11 plates. December, 14, 1878.
1880. Report on the Results of Dredging, etc. VI. Report on the Corals and Antipatharia. By L. F. Pourtalès. pp. 26. 3 plates. February, 1880.
1880. Report on the Florida Reefs. By Louis Agassiz. Accompanied by Illustrations of Florida Corals, from drawings by A. Sonrel, Burkhardt, A. Agassiz, and Roetter. With an Explanation of the Plates, by L. F. Pourtalès. Published by permission of A. D. Bache and Carlile P. Patterson, Superintendent of the U. S. Coast Survey. pp. 61. 23 plates. May, 1880.

In Appleton's Encyclopædia the following articles : —

Atlantic Ocean, Vol. II.—Dredging (Deep-Sea), Vol. VI.—Galapagos, Vol. VII.—Indian Ocean, Vol. IX.—Juan Fernandez, Vol. IX.—Magellan, Straits of, Vol. X.—Mediterranean Sea, Vol. XI.—Pacific Ocean, Vol. XII.—Polar Seas (geography), Vol. XIII.

## BENJAMIN PEIRCE.

BENJAMIN PEIRCE was born in Salem, Mass., on the 4th day of April, 1809, and he died at Cambridge, on the 6th day of October, 1880.

In his early years he had the good fortune to come under the influence of Doctor Nathaniel Bowditch. It is said that their first acquaintance was made while Doctor Bowditch's son Ingersoll and young Peirce were schoolmates. Ingersoll showed his comrade a solution which his father had prepared of a problem that the boys had been at work upon. Some error, real or conceived, was pointed out in the work, which was reported by Ingersoll to his father. "Bring me that boy who corrects my mathematics!" was the invitation to an acquaintance, the importance of which in Professor Peirce's own estimation is told in the dedication, more than thirty years later, of his "Analytic Mechanics" "to the cherished and revered memory of my Master in Science, Nathaniel Bowditch, the father of American Geometry."

Peirce entered Harvard College in 1825. As Doctor Bowditch was now in Boston, having removed from Salem in 1823, and was preparing the first volume of his translation of Laplace's "Mécanique Céleste" for the press, it followed almost as a matter of course that the college student was more influenced in his studies by him than by



the college course. Doctor Bowditch's first volume was completed, and the second entered for copyright, in 1829, the year of Peirce's graduation; and the proof-sheets were regularly read by him.

After graduation, two years were spent by Professor Peirce in teaching at Northampton. In 1831 he was appointed Tutor in Harvard College, and in 1833 was made Professor of Mathematics and Natural Philosophy.

The earlier years of his professorship were fruitful as to publication, principally in a series of text-books for use in college. The first that appeared was a "Treatise on Sound" in 1836, which was based upon Herschel's work in the "Encyclopædia Metropolitana," but with very important changes. The bibliography of the subject in the Introduction is of permanent value. This was followed in 1837 by his "Plane and Solid Geometry," and a "Treatise on Algebra," and in 1840 by a Treatise on "Plane and Spherical Trigonometry."

A work on "Curves, Functions, and Forces" was begun in 1841 by the publication of a volume on "Analytical Geometry and Differential Calculus." A second volume, on the "Calculus of Imaginaries, Residual Calculus, and Integral Calculus," appeared in 1846. As the word "forces" in the title shows, he intended to complete this work by a third volume on the "Calculus of Variations, and on Analytical Mechanics, with its Applications," but in this form it was never done.

Instead of this, however, and so to be mentioned in this place, though not properly a text-book, there appeared in 1855 the "Analytic Mechanics" in a quarto form, a work that more adequately expresses Professor Peirce's peculiar power than any other of his productions, with perhaps one exception.

In all of these books he departed not a little from the beaten path. In geometry the idea of direction was made the basis of the theory of parallels. Infinites and infinitesimals are introduced, along with the axiom, "Infinitely small quantities may be neglected." The demonstrations are given only in outline, being in respect of fulness the entire opposite of Euclid. A like brevity is characteristic of the other books, and in fact of everything mathematical that Professor Peirce ever wrote. He used a notation to which he gave much thought, by which his formulas were more concise than they could easily be made with the usual symbols. The Integral Calculus was at the period of its appearance much in advance of similar works, especially in the treatment of differential equations. It is an excellent example of Professor Peirce's concise and logical style.

The "Analytic Mechanics" was rather a treatise than a text-

book. In it Professor Peirce set forth the general principles and methods of the science as a branch of mathematical theory, and embodied in a systematic treatise the latest and best methods and forms of conceptions of the great geometers. He aimed to reduce them to their utmost simplicity by freeing them from every superfluous element. He made free use of the idea of the *potential*, developing nearly the whole subject from it. Determinants are used regularly as a standing instrument of analysis, and especially in the integration of the differential equations of motion. Both of these features, as well as Jacobi's method of integration by his principle of the last multiplier, were at the time new in English treatises.

The whole volume is marked by a directness of thought and a brevity of expression which make it difficult reading for those who have been accustomed only to the usual forms of notation and reasoning, and who do not read the book in course from the beginning. Several of the chapters are made peculiarly interesting by the development of a large number of special problems as particular cases of general theorems. In his later years the author often said he wanted to rewrite the "Analytic Mechanics" and introduce quaternions into it.

In 1842 Professor Peirce published, in connection with Professor Lovering, four numbers of the "Cambridge Miscellany," a quarterly journal devoted to mathematics, physics, and astronomy.

In the same year he assumed the care of the mathematical part of the "American Almanac," ten volumes of which were prepared by him. In one of these (1847) he published a list of the known orbits of comets, arranged in convenient form, to which he added to the usual cometic catalogue several approximate orbits computed by him for historic comets that had been imperfectly observed.

In 1849 Congress established a Bureau for the publication of the "American Ephemeris and Nautical Almanac," under the superintendence of Lieutenant (afterwards Admiral) Davis. Professor Peirce was at once appointed Consulting Astronomer. In this capacity he prepared and published, in 1853, his "Tables of the Moon," which have been used in making the "Ephemeris" up to the volume for the year 1883. In co-operation with Lieutenant Davis, he designed the form and general plan of the Ephemeris, and he decided upon all the coefficients to be used. He commenced a revision of the theory of the planets, especially the four outer ones; but this seems not to have been carried to serviceable results, if we except certain separate communications to this Academy. He retained the position of Con-

sulting Astronomer until 1867. The high place which the "American Ephemeris" has ever held among like publications is greatly due to the character given to it by Professor Peirce in these its earliest years.

When, in 1846, Galle discovered the planet Neptune in the place pointed out to him by Leverrier, Professor Peirce took the liveliest interest in the admirable researches of Leverrier and Adams. He entered with zest into all the questions which were thus raised. What is the orbit of the new planet? What its mass? How much do they differ from the assigned orbits and masses? Does the new planet explain all the irregularities of Uranus? Did the data lead necessarily to the assigned place, and to it alone?

The results of his investigations were at various times given to this Academy, but more especially on the 4th of April, 1848. He then gave the perturbations of longitude and radius vector of Uranus by Neptune, and announced that Neptune and either of the two hypothetical planets of Leverrier and Adams would equally explain the observations of Uranus, within reasonable limits of error.

Leverrier had proposed to himself to solve the following problem. From the observed irregularities of the planet Uranus to compute the elements of the orbit of an assumed exterior planet that has caused these irregularities. He ought perhaps to have limited himself to the other problem, to which he gave so correct an answer, where among the stars astronomers must look in order to see the disturbing body. The elements of the orbit could be had from observations when once the planet was seen. He found for the unknown planet an orbit and a mass by processes that will always command the admiration of men; and the place in that orbit, as is well known, was less than one degree, as seen from the earth, from the actual place where Galle found Neptune.

Yet Professor Peirce declared that Leverrier's geometric planet and Neptune were not the same bodies. He praised without question the work of Leverrier and of Adams, asserting for them their right to all the praise and *éclat* which the world had given them. But Leverrier had distinctly stated that the planet which disturbed Uranus could not be at a less mean distance from the sun than 35; that is, that no planet that was within this distance could cause the observed irregularities of the motion of Uranus. Neptune, however, is at a distance of only 30, and does account for the perturbations of Uranus.

In this and in other communications Professor Peirce claimed that the perturbations changed their character at the points where the mean

motions had the ratios 2:5 and 1:2, and that the reasonings of Leverrier were thereby vitiated. Not a little controversy has come from these papers of Professor Peirce; and we cannot say that the last word in regard to the question has even yet been spoken. As is not unusual in like discussions, there is probably a portion of truth and a portion of error with either party. Leverrier and Adams each, as Professor Peirce admits, did point out correctly a place where a planet should be looked for, and assigned paths which that planet could have been travelling for more than one hundred and twenty years previously, and have caused the observed irregularities. Yet the elements of that planet's orbit and its mass and those of Neptune differ widely enough to justify the assertion that *they* were not correctly given.

On the other hand, astronomers will not probably agree with Professor Peirce in regarding the change of character of the perturbations when the mean motions of the new planet and of Uranus pass through the exact ratios 3:5 and 1:2 as of vital importance. In the usual form of development these fractions do indeed make certain terms infinite. That belongs, however, to the form of the development, not to the perturbations. In solving the question, "Where is the disturbing body?" the solution need not have involved these forms; and it has not been shown that they entered into the work of either Leverrier or Adams in such a way as to vitiate it.

That the problem was really indeterminate has been steadily held by Professor Peirce. In January, 1878, he read to this Academy a paper, which has not been published, and the conclusions of which, therefore, will not compel the assent of astronomers until some one else shall have gone over the same questions. He showed a chart of the plane of the ecliptic with the orbits of Uranus and Neptune, and having those parts of the plane shaded within any part of which a planet of arbitrary mass might have been situated in September, 1846, and yet have caused, in the preceding years, the observed irregularities in the motions of Uranus, within reasonable limits of error. With a circular orbit, a large fraction (more than one half) of the ecliptic, as seen from the earth, contained some of the shaded portions. If an eccentricity not greater than one tenth be allowed, the region was greatly enlarged. While, therefore, the solutions of Leverrier and Adams gave a place and a path that explained the disturbances, the problem in its nature was not, he claimed, one having a single answer, or even a finite number of answers.

In 1852, Professor Bache, then Superintendent of the United States

Coast Survey, induced Professor Peirce to take up the subject of the longitude determinations in the Survey. As a result, there appeared in the successive volumes of the "Coast Survey Reports," communications from him upon the several questions that arise in the treatment of that subject. The most noteworthy referred to the determination of our longitude from Greenwich, since local differences were determined by the telegraphic method. The whole subject of errors of observations, the law of facility of error which is assumed in the method of least squares, its limits and defects, and the habits of observers, were carefully examined. The method of occultations was decided to admit of greater accuracy than any other that was then available, and the occultations of the Pleiades to furnish the most convenient means of its application. Formulæ and tables were prepared, old observations collected, and new ones made to apply this method. The question of our longitude is now, thanks to the ocean telegraph, one of history; but the questions of errors in observing, which Professor Peirce so thoroughly treated, will always be of practical import.

It seems as though there was a connection between this engagement with the Coast Survey and the appearance, in July, 1852, in Gould's "Astronomical Journal," of an article by Professor Peirce, entitled, "Criterion for the Rejection of Doubtful Observations." His object was to solve this problem: There being given certain observations, of which the greater part is to be regarded as normal, and subject to the ordinary law of error adopted in the method of least squares, while a smaller unknown portion is abnormal, and subject to some obscure source of error, to ascertain the most probable hypothesis as to the partition of the observations into normal and abnormal. This method or rule given for deciding whether an observation had better be left out of account has received the name, "Peirce's Criterion," and must be regarded as one of his best contributions to science. Tables for use in applying it were soon afterwards published by Dr. Gould.

The "Criterion" has been criticised by Professor (now Sir G. B.) Airy as defective in its foundation and illusory in its results; and he was even of opinion that no rule for the exclusion of an observation can be obtained by any process founded purely upon a consideration of the discordance of those observations. This position of the Astronomer Royal must be regarded as entirely untenable; for no observer hesitates to call a widely discordant observation a mistake, and to reject it (when he can find no other reason for so doing), simply because of that discordance. What the mind thus instinctively does, there must be basis at least for a rule for doing. Professor Airy's objections were

answered by Professor Winlock at the time of their appearance. The "Criterion" has been used considerably in this country, though not, perhaps, in Europe. The uniform testimony of our computers is, we believe, that it has given excellent discrimination, and that it does not come into conflict with proper judgment based upon experience. This shows the good working of it in actual practice.

That the "Criterion" has not come into use in Europe may in some degree have been due to the excessive brevity of the argument by which Professor Peirce established the equations to be used. Perhaps no one has read that argument for the first time without finding difficulty in understanding some parts of the reasoning. A want of confidence may thus have easily resulted. Professor Chauvenet has given us a simpler rule for use in rejecting a single divergent observation; but it is only an approximate solution, since one important element is left out of account. Computers need some such rule to guide them, and it would seem almost certain that "Peirce's Criterion," or possibly some modified form of it, will in time secure general acceptance. In any case, it will ever stand as the first, and as a satisfactory solution of this delicate and practically important problem of probability. At present it is the only solution we believe that claims to be complete.

After the death of Professor Bache, Professor Peirce was in 1867 made Superintendent of the United States Coast Survey, and he discharged the duties of that office for the next seven years. Soon after his appointment, he made a tour of inspection among the parties at work in the field. Notwithstanding his previous intimate relations with the survey as adviser to Professor Bache, he was very much surprised and delighted with the practical skill which many of the officers had acquired. "I recognize, at once," he said, "the masters of the profession." Unfortunately he recognized also the awkward and inefficient, and the presence of these, which even the admirable executive abilities of his predecessor had not been able to eliminate, gave him great concern. Yet he determined to hold to the broadest line of policy, and introduce no rigid discipline that might damp the ardor and spontaneity of the faithful. "The lame and the lazy are always provided for," says the adage; and in the public service they are found, practically, to have the most friends from without, because needing them most. In a scientific service like the Coast Survey, which unlike many of the departments of the civil service furnishes absolute criteria from which to judge the merits of an officer, the task of discrimination, if undertaken by a superintendent well versed in the mathematics and physics underlying the manœuvres of the surveyor, would seem to be



as easy as it is just. But it was a saying of Professor Bache, that "it would be easy enough to crush directly the men who betrayed the good repute of the service if it was not for uncles, aunts, and cousins, who proposed, in their turn, to crush him."

It was after his return from one of his earliest tours of inspection that Professor Peirce, in conversation with one of the older assistants, said he purposed to give, at least at the outset, greater freedom of action to the officers of the corps, that each might indicate the full scope of his powers and receive promotion, or give place to another according as the results of his work might determine. "The office," he said, "can add nothing to my reputation unless I can give it greater dignity by raising the standard of the service. I mean to bring the best men to the front and secure publicity to their merits, that they may feel directly responsible to the community and do their utmost for its approbation. To become the leader of a corps of distinguished men is the best thing I can do for the country, for the men themselves, and for my own reputation." This was the policy which he initiated in the Coast Survey, and its wisdom was demonstrated at once. A very large proportion of the officers appreciated his motives, caught the enthusiasm of his genius, and found a new delight in serving a master who coveted nothing, but with rare simplicity lent his own strength to secure to them the full rewards of their labors.

The most important work started by Professor Peirce, and much advanced under his direction, was the actual extension of geodetic work into the interior of the country by continuing the great diagonal arc from the vicinity of Washington to the southward and westward along the Blue Ridge, eventually to reach the Gulf of Mexico near Mobile. He also planned the important work, now in active progress, for measuring the arc of the parallel of thirty-nine degrees, to join the Atlantic and Pacific systems of triangulation; and for determining geographical positions in States having geological or topographical surveys in progress.

He conferred a very important benefit on public interests, by so enlarging the scope of the Survey as practically to extend geodetic work into the interior States.

As soon after the war as vessels and officers could be had, he renewed operations for deep-sea soundings and dredgings, and he gave earnest support and aid to all scientific work in any way related to the Survey.

While Superintendent he also took personal charge of the American expedition to Sicily, to observe the eclipse of the sun in December, 1870.



By virtue of his office he was a member of the Transit of Venus Commission, and by his suggestions and active effort he greatly aided that undertaking. Two parties from the Coast Survey were sent out by him,—one to Nagasaki, and the other to Chatham Island, to take part in the work.

The "Quaternion Analysis" of Hamilton seemed to Professor Peirce to promise a very fruitful future. "I wish I was young again," he said, "that I might get such power in using it as only a young man can get." He took great pains to interest his students in it, and in his later years formed a class for its earnest practical study, with good results. His own thought was turned especially to the logic that underlies all similar systems, and to the limits and the extensions of fundamental processes in mathematics.

At the first session of the National Academy of Sciences, in 1864, he read a paper on the elements of the mathematical theory of quality. Between 1866 and 1870 various papers were read to that Academy, or to this Academy, on "Linear Algebra," "Algebras," "Limitations and Conditions of Associated Linear Algebras," "Quadruple Linear Associative Algebra," etc. These papers were not printed in form as read, but instead in 1870-71 appeared his "Linear Associative Algebra."

His own feeling about this contribution to science is expressed in the salutatory to his friends: "This work has been the pleasantest mathematical effort of my life. In no other have I seemed to myself to have received so full a reward for my mental labor in the novelty and breadth of the results."

An analysis of this treatise was given by Doctor Spottiswoode to the London Mathematical Society, which is characterized by Professor Peirce as "fine, generous, and complete." Such an analysis can only come from one who has made a special study of the laws of mathematical thought. To some mathematicians, and other men of science, it may yet be a question, if the time has come for them to say with entire certainty whether this work is to share the fate of Plato's barren speculations about numbers, or to become the solid basis of a wide extension of the laws of our thinking. Those who have thought most on the course which contemporary mathematical science is taking will probably agree that the new ground thus broken can hardly fail to bring forth precious fruit in the future by adding to the powers of mathematics as an instrument.

In any case, the Associative Algebra can never lose its value as an important and most beautiful addition to Ideal Mathematics, and must

ever remain a monument to the comprehensive grasp of thought and analytical genius of its author.

Professor Peirce defines mathematics as the science which draws necessary conclusions. Algebra is formal mathematics. Addition is taken to express a mixture, or mere union of elements, independently of any mutual action which might arise if they were to be mixed in reality. From this definition, the commutative character of addition necessarily follows. Multiplication is no further defined than as an operation distributive with reference to addition; but the only algebras treated are those whose multiplication is associative. The subject is further limited to linear algebras, that is, to such as contain only a finite number of lineally independent expressions; so that every quantity considered may be put under the form,

$$ai + bj + ck + \text{etc.}$$

where  $i, j, k$ , are peculiar units, limited in number; while  $a, b, c$ , are scalars, — a term borrowed from the language of quaternions, but here used in a modified sense to include, not merely the reals, but also the imaginaries, of ordinary algebra. A variety of highly general theorems are given, extending to all linear associative algebras. The author next introduces the conception of a pure algebra, as contradistinguished from one which is virtually equivalent to a combination of several. Methods are developed for finding all such pure algebras of any order. Finally, he obtains the complete series of multiplication-tables of these algebras up to the fifth order, together with the most important class of the sixth order. They are in number as follows:—

|                 |    |
|-----------------|----|
| Single Algebras | 2  |
| Double “        | 3  |
| Triple “        | 5  |
| Quadruple “     | 18 |
| Quintruple “    | 70 |
| Sextuple “      | 65 |

Professor Peirce never made any extended study of the possible applications of his algebras; he was far from thinking, however, that their utility was dependent upon finding interpretations for them; on the contrary, he showed that certain of them could be advantageously employed, without any interpretation, in the treatment of partial differential equations like that of Laplace.

He read to this Academy in May, 1875, a memoir “On the Uses and Transformations of Linear Algebra,” which is, we believe, his only published addition to the principal treatise. He had also

made some progress in the investigation of the laws of *non-associative* algebras.

Professor Peirce could not fail to be interested in all questions that concern the equilibrium, the history, and the development of the solar system. At first he was loth to accept the nebular hypothesis in any form. But the results of his studies led him, at last, to defend its main propositions as the true laws of creation.

The rings of Saturn are of prime import in any explanation of planetary development. The discovery by Professor Bond in 1850 of the dusky ring, and his announcement of reasons for believing that the rings were fluid, multiple, and variable in number, led Professor Peirce to take up the mathematical theory of the rings. He announced as the result of his analysis that the rings could not be solid, that a fluid ring could not have its centre of gravity controlled by its primary, and that it must be supported by the satellites. The principles of the solution were indicated in an article, published in "Gould's Astronomical Journal" in 1851. At different times in the following years some portions of his theoretical treatment of the problem were published. The mathematical possibility of a large number of narrow solid rings was admitted. In the "Memoirs of the National Academy of Sciences" he published, in 1866, the formulas for the potentials and attractions of a ring. This problem has peculiar interest, from the mode of development of the formulas.

The place of comets in the solar system was a subject of his thought even earlier than the rings of Saturn. The discussions and the computation of orbits of various comets in the years 1846-1849, were followed in the latter year by an argument that the comets must have always been parts of the solar system.

In 1859 he applied the theory of solar repulsion of the matter of the comets' tails to the observed form of the tail of Donati's comet, and deduced the strength of the repulsive forces that drove off the nebulous matter.

In 1861 he made a communication to this Academy, suggesting the meteors as a cause of the acceleration of the moon's mean motion. The paper was not printed, and it does not appear whether he referred to the direct impact of the meteors upon the moon, or to the resistance due to the action of the moon in turning the meteors out of their paths. Probably he included both causes, since each has the effect, to a limited degree, of a resisting medium.

In the last two years of his life he presented to this Academy several communications upon the internal structure of the earth, and the

meteoric constitution of the universe. Especially in October, 1879, he gave a series of eight propositions in *Cosmical Physics*. At an informal scientific meeting at Harvard University he stated five others, which have been since printed in the Appendix to his "Lectures on Ideality in Science." They were given rather as a basis for criticism and discussion than as fully proved. They are founded upon the theory of Mayer, which is advocated by Sir William Thomson, that solar heat, and in part planetary heat, are supplied by the collision of meteors with the sun and planets. Small portions of matter in space cool and become invisible solid meteors. These, by their impact with the sun, produce the violent commotions of the sun's surface. A portion of the earth's heat comes from the sun, another portion directly from the impact of meteors with the earth's atmosphere. The two portions, he afterwards shows, are equal.

These views are developed more fully in his "Lectures," recently published. The meteors, as Professor Peirce believed, come from the outer portions of the condensing solar nebula. In the course of development an outer shell was left, which furnished the matter to be collected, in small masses. The smallest become meteors, the larger comets. Their numbers are enormously great. Arranged according to perihelion distances, the number of comets or meteors coming within a given distance of the sun varies directly as the distance. The heat of Jupiter and Saturn comes from the collisions with those planets. The interior of the earth may be liquid throughout, and the limits set to the lengths of the geologic ages may reasonably be greatly extended.

Any attempt to outline the history of the solar system is sure to lead, in the present state of knowledge, into serious difficulties. Some of the positions assumed by Professor Peirce, especially Mayer's theory of the source of the sun's heat, will be contested. Even if some portions are not found true, the parts would not all fall together, and we may well leave them all to the discussion that he invited for them.

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## ASSOCIATE FELLOWS.

J. LEWIS DIMAN, D.D.

J. LEWIS DIMAN, D.D. was born at Bristol, Rhode Island, May 1, 1831. He was prepared for college in his native place, and graduated at Brown University in 1851. He subsequently spent sev-

eral years in study at German Universities, and then entered the Theological Seminary at Andover, where he graduated in 1856. In the autumn of that year he became pastor of the First Congregational Church in Fall River, and, in 1860, pastor of the Harvard Church in Brookline. In 1864 he succeeded Professor Gammell as Professor of History and Political Economy in Brown University, and filled this office till his death. Several attempts were made to secure his services at Harvard University, and a negotiation to that effect, which gave those most interested in it strong hope of success, was in progress during the last weeks of his life. He died in Providence, after a short and acute illness, on the third day of February, 1881.

It is difficult to form a just estimate of Professor Diman on account, not of the scantiness, but of the wealth of the materials for our appreciation. Like many other men who are known through the press or by the living voice, he seemed to have no specialty. But, as is the case with very few, it is because he excelled in so many departments that we cannot define his specialty. He would have won distinguished reputation by as successful work in either of several departments as he has wrought in all of them. As a preacher he had few equals, whether in elaborate thought, in the expression of devotional sentiment, in blended grace and strength of style, or in the charm of an elocution, calm and gentle, yet for this none the less forceful and effective. As a student, teacher, and writer of history, he manifested at once the patience and thoroughness of a keen investigator, the vivid imagination and lambent fancy without which the man of extensive research becomes a mere Dryasdust, and the capacity of interesting alike college classes, popular audiences, and readers of the highest intelligence and culture. In philosophy he was not only an adept, but an earnest and profound thinker; and in many of his writings there occur, on the old, yet ever new, themes that underlie all thought and being, such discussions as might make it in some quarters a subject of regret that he had not bestowed his life-work on these themes. At the same time he treated political subjects as matters, not merely of theory, but of imminent and vital practical importance, in such a way as would have befitted a man who had been embodying Christian ethics in a long and varied handling of public affairs.

This versatility, not of pursuit, but of excellence, was due in part, no doubt, to a native breadth of mental hospitality, which could neither exclude nor slight any subject or interest worthy of its genial reception, and in part to a rare capacity for continuous labor, and to a life so ordered, equally by external conditions and by his own wise

economy of time, as to afford large opportunity for profound and concentrated intellectual industry.

So far as we know, Professor Diman has published little except occasional sermons, lectures, and addresses, which, however, are not fugitive or ephemeral, except in form. He must have left full courses of lectures and other writings, which will be gladly welcomed by his many friends and admirers, and cannot but extend his reputation in time and space far beyond the limits prescribed to it by his own modesty and reticence.

Professor Diman was respected, esteemed, and beloved by all who knew him. In the city of his residence he was well known as the friend of the poor, the wise counsellor and ready helper in every good work, the pioneer in every movement for the instruction, elevation, and improvement of the community. In all the relations of life, and in his whole social intercourse, he had the manners, bore the character, and breathed the spirit, of the "highest style of man," — the Christian gentleman.

#### SAMUEL SHERMAN HALDEMAN.\*

PROFESSOR SAMUEL SHERMAN HALDEMAN died on Friday, the 17th of September, at his home in Chickies, Pennsylvania, aged sixty-eight years. He was born near Columbia, Pa., in 1812, and graduated at Dickinson College in 1830. In 1836 he was connected with the Geological Survey of New Jersey, and the following year with that of Pennsylvania. He was Professor of Natural History in the University of Pennsylvania from 1851 to 1855, and in 1855 took the same chair in Delaware College, and also that of Professor of Geology and Chemistry in the Agricultural College of Pennsylvania. He afterward became Professor of Philology in the University of Pennsylvania. For many years he worked with great zeal and success in entomology and conchology, and published various memoirs, describing new species and illustrating the broader subject of geographical distribution. Among these are his work on the "Freshwater Mollusca of the United States," his "Zoological Contributions," and a paper on the Coleoptera Longicornia of the United States. Later he devoted himself especially to philological studies, phonetics, and orthography. His "Analytic Orthography" obtained for him in England the Trevelyan prize in 1858. He paid much attention to the Indian languages of North

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\* From the American Journal of Science.



America and their pronunciation. The diversity of his tastes and learning is further shown in his "Tours of a Chess Knight" (1864), a volume of ninety pages, illustrated with 114 figures, and containing a bibliography including sixty references.

## JAMES CRAIG WATSON.

JAMES CRAIG WATSON was born Jan. 28, 1838, in the part of Canada now known as the Province of Ontario. His family removed in 1850 to Ann Arbor, Michigan, where he was prepared for college, entering the University of Michigan in 1853, and graduating in 1857. His collegiate career was highly successful in the department of languages, as well as in that of mathematics; but before its close he had already formed a decided taste for astronomical pursuits, and had actually entered upon the course of observation in which he was afterwards distinguished. He discovered a comet April 29, 1856, and the asteroid Aglaia (found a few days previously in Europe) on October 20, 1857. He is said to have read the whole of the "*Mécanique Céleste*" before the end of his Junior year in college, although a portion of his time was occupied in earning the means requisite to provide in part for his expenses.

After completing his college course, he entered the Ann Arbor Observatory as an assistant, and two years later, on the temporary retirement of Dr. Brünnow, succeeded him in the management of the institution. From 1860 to 1863, Dr. Brünnow was again Director of the Observatory, Professor Watson having been transferred to the department of Physics. At the end of this interval, he returned to the Observatory, which he continued to direct till 1879. During his term of office, he made the numerous discoveries of asteroids (twenty-two of these planets being first observed by him) which rendered his name familiar to astronomers and to the public at large. In 1869 appeared his great work on "*Theoretical Astronomy*," then and ever since the only text-book upon the subject of which it treats which can be called complete, in the sense of comprising in one volume of moderate dimensions all the knowledge essential for the computation of planetary and cometary orbits by modern methods, and including the topic of perturbations. It was of course impossible for the author to describe, or even to enumerate, all the special methods occasionally brought into use for the solution of these problems; but his unusual mathematical attainments, and the quickness and penetration of his intellect enabled him to succeed in selecting, arranging, and, where



necessary, improving the material to be included in his work, in such a manner as to produce a most valuable result. Besides this important contribution to the means of instruction in astronomy, he frequently sent communications to scientific periodicals.

Professor Watson was also known as an observer of special phenomena. He observed the total solar eclipses of 1869, 1870, and 1878, at the respective stations of Mt. Pleasant, Iowa, Carlentini, Sicily, and Separation, Wyoming Territory; and also the transit of Venus in 1874, at Peking, China (where he incidentally discovered an asteroid, to which he assigned the Chinese name, "Juewa," in commemoration of the place of its discovery). During the eclipse of 1878, Professor Watson found two objects which he considered to be intra-mercurial planets. In 1879 he accepted the position of Director of the Washburn Observatory at Madison, Wisconsin, where, with the aid of more powerful instruments than had previously been at his disposal, he hoped to confirm the existence of the planets found the year before, and to undertake a search for other objects of interest. But towards the end of 1880, while he was engaged in superintending the ingenious arrangements which he had devised for these purposes, a neglected cold suddenly assumed a fatal form, and terminated his earthly labors on the morning of Nov. 23.

As a man of business, Professor Watson was endowed with the acuteness and energy which distinguished him as an astronomer. He was long the Actuary of the Michigan Mutual Life Insurance Company, and filled that office with great success. Beginning life without property, he had acquired before his death a handsome fortune, of which he intended to avail himself in forwarding the astronomical researches of his later years. The sudden close of his life, at the moment when his opportunities for scientific inquiries had just been greatly enlarged, is a serious misfortune to the cause of astronomy, as well as to his numerous friends; for it cannot be doubted that his extraordinary activity and energy, combined with his capacity as a mathematician and his ingenuity as an inventor, would have continued to raise him in the estimation of the scientific world, and to produce interesting additions to our knowledge of the physical universe.

## FOREIGN HONORARY MEMBERS.

## THOMAS CARLYLE.

THE death of Mr. CARLYLE takes from the roll of our Foreign Honorary Members one whose genius received its first confident recognition in our own city, and whose influence during the whole period of his literary career was felt not less widely, or less powerfully, in this country than in his own. In losing him, English literature in the nineteenth century loses its most conspicuous figure.

The roots of his vigorous nature struck deep in his native soil. His most marked qualities, both moral and intellectual, grew from a sturdy stock. His ancestry were of the best humble Scotch blood. The account which he has given of his home in his Memoir of his Father is the counterpart of the picture of domestic simplicity and piety in Burns's "Cotter's Saturday Night." The old tradition of Scotch manliness and godliness survived with full force in him. The stern integrity, the strict sincerity, the confident independence of the Protestantism of Scotland formed the foundations of his character. He held substantially through his long life to the faith of his fathers, under a changed form, but with little change of essential principle.

To a clear intelligence and a strong understanding were united in him rare gifts of perception, of humor, and of imagination, and all were subordinated to a deep moral sentiment. The exceptionally definite individuality of his temperament and genius displayed itself not infrequently in what seemed like wilfulness of opinion, and in actual exaggeration of utterance, which hindered the recognition of the morality that lay behind. But this prevailing moral sense gave real consistency to his judgments, and informed the body of his teaching from first to last with a single spirit.

It has been often charged against him, especially of late, that the sum of his social doctrine is expressed in the aphorism that "might makes right." But the charge has no truth. His doctrine, as he himself asserted, and as all who have more than a superficial acquaintance with his work will admit, is precisely the reverse of this. "Right makes might," is the lesson he enforces. The only real might is moral. Cromwell, Frederick, the hero, whoever he may be, exercises authority in virtue of a moral claim. All power that asserts any other than a moral validity is contrary to the permanent order of society, is transient, is self-destructive. In the application of this

doctrine Carlyle may have been at times in error; but the principle itself is that on which the order of the world is dependent.

Carlyle judged the prevailing tendencies of modern society severely. He saw earlier and more clearly than any other writer of influence the inherent dangers of absolute democracy, and the weakness of the pure democratic system if adopted as the ultimate form of human society. He had no belief in the extension of the doctrine of the rights of man till it becomes subversive of the distinctions between good and bad, intelligent and ignorant. He had no sympathy with the modern optimistic temper, which believes some vague entity called "the people" to be possessed by nature of all virtue.

The great debt of the past generation, and of our own, to Mr. Carlyle is not so much for any specific piece of work as for the general influence of his life and writings in promoting the spirit of intellectual independence and integrity. In this respect his influence has been powerful, and is likely to be permanent.

His feeling to this country, which he had given us at times some reason to question, has been shown in his bequest, with words of memorable significance, of a portion of his books to the library of Harvard College.

The Academy feels its own lustre diminished by the striking off of so illustrious a name from its rolls.

#### WILLIAM HALLOWES MILLER.

WILLIAM HALLOWES MILLER, who was elected Foreign Honorary Member of this Academy in the place of C. F. Naumann, May 26, 1874, died at his residence in Cambridge, England, on the 20th of May, 1880, at the age of seventy-nine, having been born at Velindre in Wales, April 6, 1801. His life was singularly uneventful even for a scholar. Graduating with mathematical honors at Cambridge in 1826, he became a fellow of his college (St. John's) in 1829, and was elected Professor of Mineralogy in the University in 1832. Amidst the calm and elegant associations of this ancient English university, Miller passed a long and tranquil life, — crowded with useful labors, honored by the respect and love of his associates, and blessed by congenial family ties. This quiet student life was exactly suited to his nature, which shunned the bustle and unrest of our modern world. For relaxation even he loved to seek the retired valleys of the Eastern

Alps; and the description which he once gave to the writer, of himself sitting at the side of his wife amidst the grand scenery, intent on developing crystallographic formulæ while the accomplished artist traced the magnificent outlines of the Dolomite mountains, was a beautiful idyl of science.

Miller's activities, however, were not confined to the University. In 1838 he became a Fellow of the Royal Society, and in 1856 he was appointed its Foreign Secretary, — a post for which he was eminently fitted and which he filled for many years. In 1843 he was selected one of a committee to superintend the construction of the new Parliamentary standards of length and weight, to replace those which had been lost in the fire which consumed the Houses of Parliament in 1834, and to Professor Miller was confided the construction of the new standard of weight. His work on this important committee, described in an extended paper published in the *Philosophical Transactions* for 1856, was a model of conscientious investigation and scientific accuracy. Professor Miller was subsequently a member of a new Royal Commission for "examining into and reporting on the state of the secondary standards, and for considering every question which could affect the primary, secondary, and local standards"; and in 1870 he was appointed a member of the "Commission Internationale du Mètre." His services on this commission were of great value, and it has been said that "there was no member whose opinions had greater weight in influencing a decision upon any intricate and delicate question."

Valuable, however, as were Professor Miller's public services on these various commissions, his chief work was at the University. His teacher, Dr. William Whewell, — afterwards the Master of Trinity College, — was his immediate predecessor in the Professorship of Mineralogy at Cambridge. This great scholar, whose encyclopædic mind could not long be confined in so narrow a field, held the professorship only four years, but during this period he devoted himself with his usual enthusiasm to the study of crystallography, and he accomplished a most important work in attracting to the same study young Miller, who brought his mathematical training to its elucidation. It was the privilege of Professor Miller to accomplish a unique work, for the like of which a more advanced science, with its multiplicity of details, will offer few opportunities.

The foundations of crystallography had been laid long before Miller's time. Haüy is usually regarded as the founder of the science; for he first discovered the importance of cleavage, and classed the

known facts under a definite system. Taking cleavage as his guide, and assuming that the forms of cleavage were not only the *primitive forms* of crystals as a whole, but also the forms of their *integrant molecules*, he endeavored to show that all secondary forms might be derived from a few primary forms, regarded as elements of nature, by means of *decrements* of molecules at their edges. In like manner he showed that all the forms of a given mineral, like fluor-spar or calcite, might be built up from the integrant molecules by skilfully placing together the primitive forms. Haüy's dissection of crystals, in a manner which appeared to lead to their ultimate crystalline elements, gained for his system great popular attention and applause. The system was developed with great perspicuity and completeness in a work remarkable for the vivacity of its style and the felicity of its illustration. Moreover, a simple mathematical expression was given to the system, and the notation which Haüy invented to express the relation of the secondary to the primary forms, as modified and improved by Lèvy, is still used by the French mineralogists.

The system of Haüy, however, was highly artificial, and only prepared the way for a simpler and more general expression of the facts. The German crystallographer, Weiss, seems to be the first to have recognized the truth that the decrements of Haüy were merely a mechanical mode of representing the fact that all the secondary faces of a crystal make intercepts on the edges of the primitive form which are simple multiples of each other; and this general conception, once gained, it was soon seen that these ratios could be as simply measured on the axes of symmetry of the crystal as on the edges of the fundamental forms; and, moreover, that when crystal forms are viewed in their relation to these axes a more general law becomes evident, and the artificial distinction between primary and secondary forms disappears.

Thus became slowly evolved the conception of a crystal as a group of similar planes symmetrically disposed around certain definite and obvious systems of axes, and so placed that the intercepts, or parameters, on these axes bore to each other a simple numerical ratio. Representing by  $a : b : c$  the ratio of the intercepts of a plane on the three axes of a crystal of a given substance, then the intercepts of every other plane of this, or of any other crystal of the same substance, conform to the general proportion  $ma : nb : pc$ , in which  $m, n, p$  are three simple whole numbers. This simple notation, devised by Weiss, expressed the fundamental law of crystallography, and the conception of a crystal as a system of planes, symmetrically distributed according to this

law, was a great advance beyond the decrements of Hüy, an advance not unlike that of astronomy from the system of vortices to the law of gravitation. Yet, as the mechanism of vortices was a natural prelude to the law of Newton, so the decrements of Hüy prepared the way for the wider views of the German crystallographers.

Whether Weiss or Mohs contributed most to advance crystallography to its more philosophical stage, it is not important here to inquire. Each of these eminent scholars did an important work in developing and diffusing the larger ideas, and in showing by their investigations that the facts of nature corresponded to the new conceptions. But to Carl Friedrich Naumann, Professor at the time in the "Bergakademie zu Freiberg," belongs the merit of first developing a complete system of theoretical crystallography based on the laws of symmetry and axial ratios. His "*Lehrbuch der reinen und angewandten Krystallographie*," published in two volumes at Leipzig in 1830, was a remarkable production, and seemed to grasp the whole theory of the external forms of crystals. Naumann used the obvious and direct methods of analytical geometry to express the quantitative relations between the parts of a crystal; and although his methods are often unnecessarily prolix and his notation awkward, his formulæ are well adapted to calculation, and easily intelligible to persons moderately disciplined in mathematics.

But, however comprehensive and perfect in its details, the system of Naumann was cumbrous, and lacked elegance of mathematical form. This arose chiefly from the fact that the old methods of analytical geometry were unsuited to the problems of crystallography; but it resulted also from a habit of the German mind to dwell on details and give importance to systems of classification. To Naumann the six crystalline systems were as much realities of nature as were the forms of the integrant molecules to Hüy, and he failed to grasp the larger thought which includes all partial systems in one comprehensive plan.

Our late colleague, Professor Miller, on the other hand, had that power of mathematical generalization which enabled him to properly subordinate the parts to the whole, and to develop a system of mathematical crystallography of such simplicity and beauty of form that it leaves little to be desired. This was the great work of his life, and a work worthy of the University which had produced the "*Principia*." It was published in 1839, under the title "*A Treatise on Crystallography*;" and in 1863, the substance of the work was reproduced in a more perfect form, still more condensed and generalized, in a thin



volume of only eighty-six pages, which the author modestly called "A Tract on Crystallography."

Miller began his study of crystallography with the same materials as Naumann; but, in addition, he adopted the beautiful method of Franz Ernst Neumann of referring the faces of a crystal to the surface of a circumscribed sphere by means of radii drawn perpendicular to the faces. The points where the radii meet the spherical surface are the poles of the faces, and the arcs of great circles connecting these poles may obviously be used as a measure of the angles between the crystal faces. This invention of Neumann's was the germ of Miller's system of crystallography; for it enabled the English mathematician to apply the elegant and compendious methods of spherical trigonometry to the solution of crystallographic problems; and Professor Miller always expressed his great indebtedness to Neumann not only for this simple mode of defining the position of the faces of a crystal, but also for his method of representing the relative position of the poles of the faces on a plane surface by a beautiful application of the methods of stereographic and gnomonic projection. This method of representing a crystal shows very clearly the relations of the parts, and was undoubtedly of great aid to Miller in assisting him to generalize his deductions.

From the outset, Professor Miller apprehended more clearly than any previous writer the all-embracing scope of the great law of crystallography. He opens his Treatise with its enunciation, and from this law as the fundamental principle of the subject the whole of his system of crystallography is logically developed. Beyond this, all that is peculiar to Miller's system is involved in two or three general theorems. The rest of his Treatise consists of deductions from these principles and their application to particular cases.

One of the most important of these principles, and one which in the Treatise is involved in the enunciation of the fundamental law of crystallography, is in its essence nothing but an analytical device. As we have already stated, Weiss had shown that, if  $a : b : c$  represent the ratio of the intercepts of any plane of a crystal on the three axes  $x$ ,  $y$ , and  $z$  respectively, the intercepts of any other possible plane must satisfy the proportion —

$$A : B : C = ma : nb : pc$$

in which  $m$ ,  $n$ , and  $p$  are simple whole numbers. The irrational values  $a$ ,  $b$ , and  $c$  are fundamental magnitudes for every crystalline



substance; \* and Miller called these relative magnitudes the parameters of the crystals, while he called the whole numbers,  $m$ ,  $n$ , and  $p$ , the indices of the respective planes. But, instead of writing the proportion which expresses the law of crystallography as above, he gave to it a slightly different form, thus, —

$$A : B : C = \frac{1}{h} a : \frac{1}{k} b : \frac{1}{l} c,$$

and used in his system for the indices of a plane the values  $h : k : l$ , which are also in the ratio of whole numbers, and usually of simpler whole numbers than  $m : n : p$ . This seems a small difference; for  $h k l$  in the last proportion are obviously the reciprocals of  $m n p$  in the first; but the difference, small as it is, causes a wonderful simplification of the formulæ which express the relations between the parts of a crystal. From the last proportion we derive at once

$$\frac{1}{h} \cdot \frac{a}{A} = \frac{1}{k} \cdot \frac{b}{B} = \frac{1}{l} \cdot \frac{c}{C}$$

which is the form in which Miller stated his fundamental law.

If  $P$  represents the "pole" of a face whose "indices" are  $h k l$ , that is, represents the point where the radius drawn normal to the face meets the surface of the sphere circumscribed around the crystal (the sphere of projection, as it is called), and if  $X$ ,  $Y$ ,  $Z$  represent the points where the axes of the crystal meet the same spherical surface, † then it is evident that  $XY$ ,  $XZ$ , and  $YZ$  are the arcs of great circles, which measure the inclination of the axes to each other, and that  $PX$ ,  $PY$ , and  $PZ$  are arcs of other great circles, which measure the inclination of the plane ( $h k l$ ) on planes normal to the respective axes; and, also, that these several arcs form the sides of spherical triangles thus drawn on the sphere of projection. Now, it is very easily shown that

$$\frac{a}{h} \cos PX = \frac{b}{k} \cos PY = \frac{c}{l} \cos PZ$$

and by means of this theorem we are able to reduce a great many problems of crystallography to the solution of spherical triangles.

\* For example, the native crystals of sulphur have  $a : b : c = 1 : 2.340 : 1.233$ ,  
 Crystals of gypsum have  $a : b : c = 1 : 0.413 : 0.691$ ,  
 Crystals of tin stone have  $a : b : c = 1 : 1 : 0.6724$ ,  
 And crystals of common salt have  $a : b : c = 1 : 1 : 1$ .

† The origin of the axes is always taken as the centre of the sphere of projection.

Another very large class of problems in crystallography is based on the relation of faces in a zone; that is of faces which are all parallel to one line called the zone axis, and whose mutual intersections, therefore, are all parallel to each other. If now  $hkl$  and  $pqr$  are the indices of any two planes of a zone (not parallel to each other) any other plane in the same zone must fulfil the condition expressed by the simple equation

$$u\,u + v\,v + w\,w = 0$$

where  $u\,v$  and  $w$  are the indices of the third plane and  $u\,v\,w$  have the values

$$u = kr - lq \quad v = lp - hr \quad w = hq - kp$$

Since  $hkl$  and  $pqr$  are whole numbers, it is evident that  $u\,v\,w$  must also be whole numbers and these quantities are called the indices of the zone. The three whole numbers which are the indices of a plane when written in succession serve as a very convenient symbol of that plane, and represent to the crystallographer all its relations; and in like manner Miller used the indices of a zone enclosed in brackets as the symbol of that zone. Thus 123, 531, 010 are symbols of planes, and [111], [213], [001] symbols of zones.

An additional theorem enables us to calculate the symbols of a fourth plane in a zone when the angular distances between the four planes and the symbols of three of them are known, but this problem cannot be made intelligible with a few words.

The few propositions to which we have referred involve all that is essential and peculiar to the system of Professor Miller. These given, and the rest could be at once developed by any scholar who was familiar with the facts of crystallography; and the circumstance that its essential features can be so briefly stated is sufficient to show how exceedingly simple the system is. At the same time, it is wonderfully comprehensive, and the student who has mastered it feels that it presents to him in one grand view the entire scheme of crystal forms, and that it greatly helps him to comprehend the scheme as a whole, and not simply as the sum of certain distinct parts. So felt Professor Miller himself; and, while he regarded the six systems of crystals of the German crystallographers as natural divisions of the field, he considered that they were bounded by artificial lines which have no deeper significance than the boundary lines on a map. How great the unfolding of the science from Haüy to Miller, and yet now we can see the great fundamental ideas shining through the obscurity from the first. What we now call the parameters of a crystal were to Haüy the funda-

mental dimensions of his "integrant molecules," our indices were his "decrements," and our conceptions of symmetry his "fundamental forms." There has been nothing peculiar, however, in the growth of crystallography. This growth has followed the usual order of science, and here as elsewhere the early, gross, material conceptions have been the stepping-stones by which men rose to higher things. In sciences like chemistry, which are obviously still in the earlier stages of their development, it would be well if students would bear in mind this truth of history, and not attach undue importance to structural formulæ and similar mechanical devices, which, although useful for aiding the memory, are simply hinderances to progress as soon as the necessity of such assistance is passed. And when the life of a great master of science has ended, it is well to look back over the road he has travelled and while we take courage in his success consider well the lesson which his experience has to teach; and, as progress in this world's knowledge has ever been from the gross to the spiritual, may we not rejoice as those who have a great hope?

Although the exceeding merit of the "Treatise on Crystallography" casts into the shade all that was subordinate, we must not omit to mention that Professor Miller published an early work on Hydrostatics, and numerous shorter papers on Mineralogy and Physics, which were all valuable, and constantly contained important additions to knowledge. Moreover, the "New Edition of Phillips's Mineralogy" which he published in 1852 in connection with H. J. Brooke owed its chief value to a mass of crystallographic observations which he had made with his usual accuracy and patience during many years, and there tabulated in his concise manner. As has been said by one of his associates in the Royal Society, "it is a monument to Miller's name, although he almost expunged that name from it."\* It is due to Professor Miller's memory that his works should be collated, and especially that by a suitable commentary his "Tract on Crystallography" should be made accessible to the great body of the students of physical science, who have not, as a rule, the ability or training which enables them to apprehend a generalization when solely expressed in mathematical terms. The very merits of Professor Miller's book as a scientific work renders it very difficult to the average student, although it only involves the simplest forms of algebra and trigonometry.

Independence, breadth, accuracy, simplicity, humility, courtesy, are

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\* Obituary Notices from the Proceedings of the Royal Society, No. 206, 1880, to which the writer has been indebted for several biographical details.

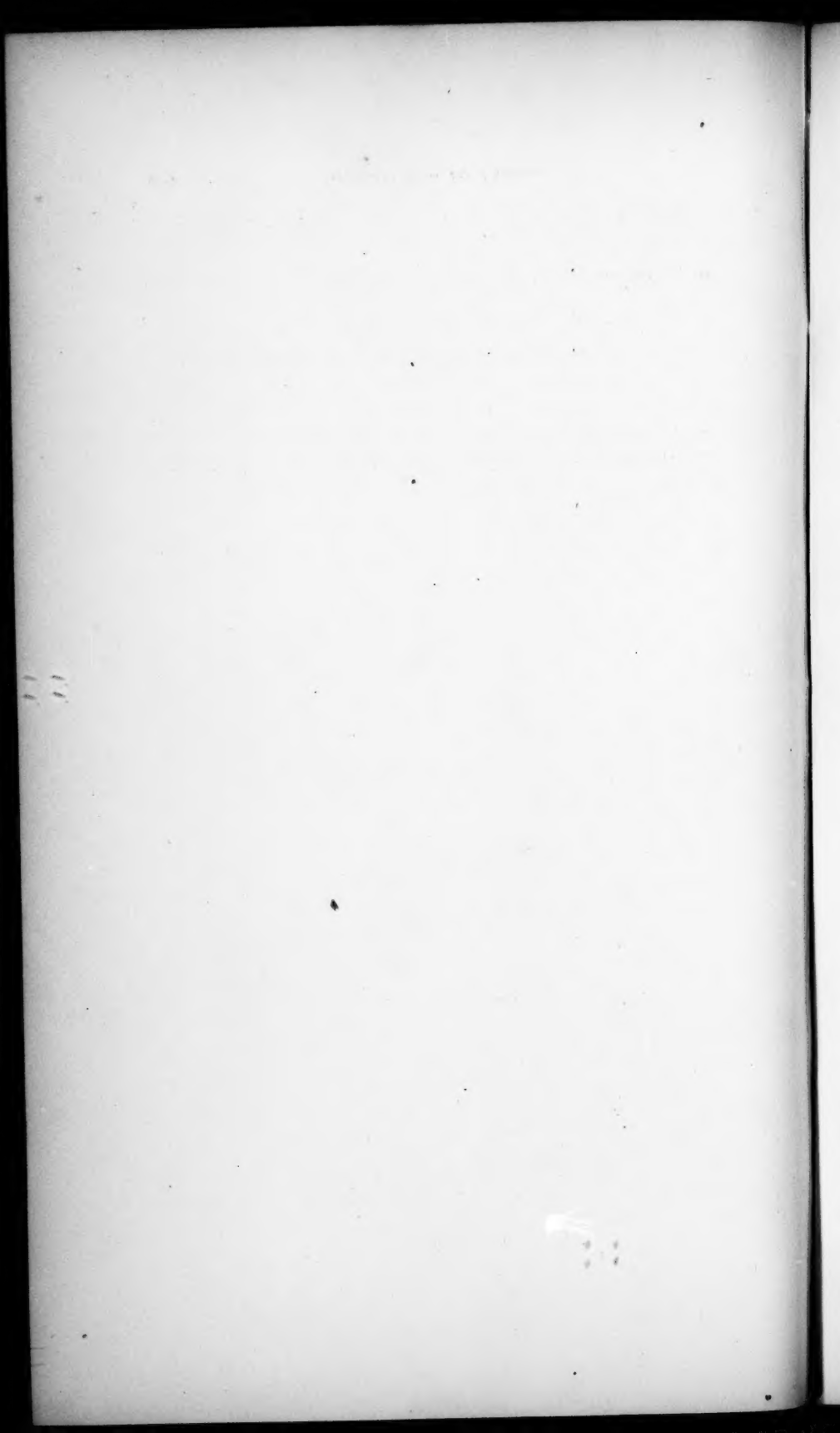
luminous words which express the character of Professor Miller. In his genial presence the young student felt encouraged to express his immature thoughts, which were sure to be treated with consideration, while from a wealth of knowledge the great master made the error evident by making the truth resplendent. It was the greatest satisfaction to the inexperienced investigator when his observations had been confirmed by Professor Miller, and he was never made to feel discouraged when his mistakes were corrected. The writer of this notice regards it as one of the great privileges of his youth, and one of the most important elements of his education, to have been the recipient of the courtesies and counsel of three great English men of science, who have always been "his own ideal knights," and these noble knights were Faraday, Graham, and Miller.

#### CHRISTIAN AUGUST FRIEDRICH PETERS.

CHRISTIAN AUGUST FRIEDRICH PETERS was born in Hamburg, Sept. 7, 1806. His father, whose circumstances did not allow him to provide a school education for his sons, early recognized their mathematical talents, and did his best to procure books to assist their studies. The eldest son, the subject of this notice, obtained employment early in life from Professor Schumacher, the Director of the Altona Observatory. After pursuing his studies and his labors at Königsberg and Hamburg, he was appointed in 1839 to a position in the newly established Observatory at Pulkowa, near St. Petersburg. Here, in the course of the following ten years, he accomplished much which has made his name well known ever since to all astronomers. His most important single work was perhaps the new determination of the constant of nutation; but many other productions of the same period, original and critical, attest his astronomical skill and learning. In 1849 he was appointed Professor of Astronomy at Königsberg, where he published his treatise on the proper motion of Sirius. He subsequently (1854) took charge of the Altona Observatory (removed in 1872 to Kiel), and occupied this position at the time of his death, which occurred, after a severe illness of several months, on May 8, 1880.

At Altona, and afterwards at Kiel, he conducted the "Astronomische Nachrichten," which continued under his management, as before, to be the principal medium for the exchange of information and suggestions by the astronomers of all civilized nations. His own work in the latter years of his life was mainly geodetic.

Since the last report, the Academy has received an accession of seven new members: three Resident Fellows, John R. Edmands, Henry W. Haynes, and Henry P. Kidder; four Foreign Honorary Members, Arthur Auwers in place of C. A. F. Peters, M. P. E. Berthelot in place of J. C. Maxwell, A. L. O. L. Des Cloizeaux in place of W. H. Miller and C. E. Brown-Séguard. On the other hand, John Fiske and Theophilus Parsons have resigned their fellowships. The list of the Academy corrected to the date of this report is hereto added. It includes 185 Resident Fellows, 90 Associate Fellows, and 73 Foreign Honorary Members.



# LIST

## OF THE FELLOWS AND FOREIGN HONORARY MEMBERS.

### FELLOWS.—185.

(Number limited to two hundred.)

#### CLASS I.—*Mathematical and Physical Sciences.*—62.

##### SECTION I.—6.

###### *Mathematics.*

|                    |            |
|--------------------|------------|
| William E. Byerly, | Cambridge. |
| Benjamin A. Gould, | Cambridge. |
| Gustavus Hay,      | Boston.    |
| James M. Peirce,   | Cambridge. |
| John D. Runkle,    | Brookline. |
| Edwin P. Seaver,   | Newton.    |

##### SECTION II.—11.

###### *Practical Astronomy and Geodesy.*

|                        |                |
|------------------------|----------------|
| J. Ingersoll Bowditch, | Boston.        |
| Alvan Clark,           | Cambridgeport. |
| George B. Clark,       | Cambridgeport. |
| John R. Edmands,       | Cambridge.     |
| Henry Mitchell,        | Roxbury.       |
| Robert Treat Paine,    | Brookline.     |
| Edward C. Pickering,   | Cambridge.     |
| William A. Rogers,     | Cambridge.     |
| Arthur Searle,         | Cambridge.     |
| Leopold Trouvelot,     | Cambridge.     |
| Henry L. Whiting,      | Tisbury.       |

##### SECTION III.—31.

###### *Physics and Chemistry.*

|                      |               |
|----------------------|---------------|
| John Bacon,          | Boston.       |
| A. Graham Bell,      | Boston.       |
| John H. Blake,       | Boston.       |
| Thos. Edwards Clark, | Williamstown. |
| W. S. Clark,         | Amherst.      |
| Josiah P. Cooke,     | Cambridge.    |
| James M. Crafts,     | Boston.       |
| Charles R. Cross,    | Boston.       |
| William P. Dexter,   | Roxbury.      |
| Amos E. Dolbear,     | Medford.      |
| Charles W. Eliot,    | Cambridge.    |
| Moses G. Farmer,     | Newport.      |

|                      |                |
|----------------------|----------------|
| Wolcott Gibbs,       | Boston.        |
| Frank A. Gooch,      | Cambridge.     |
| Augustus A. Hayes,   | Brookline.     |
| Henry B. Hill,       | Cambridge.     |
| N. D. C. Hodges,     | Cambridge.     |
| Eben N. Horsford,    | Cambridge.     |
| T. Sterry Hunt,      | Boston.        |
| Charles L. Jackson,  | Cambridge.     |
| Joseph Lovering,     | Cambridge.     |
| William R. Nichols,  | Boston.        |
| John M. Ordway,      | Boston.        |
| Robert H. Richards,  | Boston.        |
| Edward S. Ritchie,   | Boston.        |
| Stephen P. Sharples, | Cambridge.     |
| Francis H. Storer,   | Jamaica Plain. |
| John Trowbridge,     | Cambridge.     |
| Cyrus M. Warren,     | Brookline.     |
| Charles H. Wing,     | Boston.        |
| Edward S. Wood,      | Cambridge.     |

##### SECTION IV.—14.

###### *Technology and Engineering.*

|                      |                |
|----------------------|----------------|
| George R. Baldwin,   | Woburn.        |
| John M. Batchelder,  | Cambridge.     |
| Charles O. Boutelle, | Washington.    |
| Henry L. Eustis,     | Cambridge.     |
| James B. Francis,    | Lowell.        |
| John B. Henck,       | Boston.        |
| E. D. Leavitt, Jr.,  | Cambridgeport. |
| William R. Lee,      | Roxbury.       |
| Hiram F. Mills,      | Lawrence.      |
| Alfred P. Rockwell,  | Boston.        |
| Charles S. Storror,  | Boston.        |
| William R. Ware,     | Boston.        |
| William Watson,      | Boston.        |
| Morrill Wyman,       | Cambridge.     |



CLASS II. — *Natural and Physiological Sciences.* — 62.

## SECTION I. — 7.

*Geology, Mineralogy, and Physics of the Globe.*

|                      |            |
|----------------------|------------|
| Thomas T. Bouvé,     | Boston.    |
| William T. Brigham,  | Boston.    |
| Algernon Coolidge,   | Boston.    |
| John L. Hayes,       | Cambridge. |
| William B. Rogers,   | Boston.    |
| Nathaniel S. Shaler, | Cambridge. |
| Charles U. Shepard,  | Amherst.   |

## SECTION II. — 10.

*Botany.*

|                     |            |
|---------------------|------------|
| William G. Farlow,  | Boston.    |
| George L. Goodale,  | Cambridge. |
| Asa Gray,           | Cambridge. |
| H. H. Hunnewell,    | Wellesley. |
| Thomas P. James,    | Cambridge. |
| John A. Lowell,     | Boston.    |
| Charles S. Sargent, | Brookline. |
| Charles J. Sprague, | Boston.    |
| Edward Tuckerman,   | Amherst.   |
| Sereno Watson,      | Cambridge. |

## SECTION III. — 22.

*Zoölogy and Physiology.*

|                      |               |
|----------------------|---------------|
| Alex. E. R. Agassiz, | Cambridge.    |
| Joel A. Allen,       | Cambridge.    |
| Robert Amory,        | Brookline.    |
| Nath. E. Atwood,     | Provincetown. |
| James M. Barnard,    | Boston.       |
| Henry P. Bowditch,   | Boston.       |
| Edward Burgess,      | Boston.       |
| Samuel Cabot,        | Boston.       |
| John Dean,           | Waltham.      |

|                      |            |
|----------------------|------------|
| Hermann A. Hagen,    | Cambridge. |
| Charles E. Hamlin,   | Cambridge. |
| Alpheus Hyatt,       | Cambridge. |
| William James,       | Cambridge. |
| Samuel Kneeland,     | Boston.    |
| Theodore Lyman,      | Boston.    |
| Edward S. Morse,     | Salem.     |
| Frederick W. Putnam, | Cambridge. |
| James J. Putnam,     | Boston.    |
| Samuel H. Scudder,   | Cambridge. |
| D. Humphreys Storer, | Boston.    |
| Henry Wheatland,     | Salem.     |
| James C. White,      | Boston.    |

## SECTION IV. — 23.

*Medicine and Surgery.*

|                      |             |
|----------------------|-------------|
| Samuel L. Abbot,     | Boston.     |
| Henry J. Bigelow,    | Boston.     |
| Henry I. Bowditch,   | Boston.     |
| Benjamin E. Cotting, | Roxbury.    |
| Frank W. Draper,     | Boston.     |
| Thomas Dwight,       | Boston.     |
| Robert T. Edes,      | Roxbury.    |
| Calvin Ellis,        | Boston.     |
| Charles F. Folsom,   | Boston.     |
| Richard M. Hodges,   | Boston.     |
| Oliver W. Holmes,    | Boston.     |
| Robert W. Hooper,    | Boston.     |
| Alfred Hosmer,       | Watertown.  |
| Edward Jarvis,       | Dorchester. |
| Francis Minot,       | Boston.     |
| Edward Reynolds,     | Boston.     |
| John P. Reynolds,    | Boston.     |
| Wm. L. Richardson,   | Boston.     |
| George C. Shattuck,  | Boston.     |
| J. Baxter Upham,     | Boston.     |
| Charles E. Ware,     | Boston.     |
| John C. Warren,      | Boston.     |
| Henry W. Williams,   | Boston.     |

CLASS III.—*Moral and Political Sciences.*—61.

## SECTION I.—14.

*Philosophy and Jurisprudence.*

|                        |               |
|------------------------|---------------|
| James B. Ames,         | Cambridge.    |
| Charles S. Bradley,    | Providence.   |
| Phillips Brooks,       | Boston.       |
| James F. Clarke,       | Jamaica Pl.   |
| Richard H. Dana,       | Boston.       |
| Charles C. Everett,    | Cambridge.    |
| Horace Gray,           | Boston.       |
| Laurens P. Hicock,     | Northampton.  |
| Oliver W. Holmes, Jr., | Boston.       |
| Mark Hopkins,          | Williamstown. |
| C. C. Langdell,        | Cambridge.    |
| John Lowell,           | Boston.       |
| Henry W. Paine,        | Cambridge.    |
| James B. Thayer,       | Cambridge.    |

## SECTION II.—16.

*Philology and Archæology.*

|                      |            |
|----------------------|------------|
| Ezra Abbot,          | Cambridge. |
| William S. Appleton, | Boston.    |
| William P. Atkinson, | Boston.    |
| Henry G. Denny,      | Boston.    |
| Epes S. Dixwell,     | Cambridge. |
| William Everett,     | Quincy.    |
| William W. Goodwin,  | Cambridge. |
| Ephraim W. Gurney,   | Cambridge. |
| Henry W. Haynes,     | Boston.    |
| Bennett H. Nash,     | Boston.    |
| Chandler Robbins,    | Boston.    |
| John L. Sibley,      | Cambridge. |
| E. A. Sophocles,     | Cambridge. |
| John W. White,       | Cambridge. |
| Justin Winsor,       | Cambridge. |
| Edward J. Young,     | Cambridge. |

## SECTION III.—18.

*Political Economy and History.*

|                      |            |
|----------------------|------------|
| Chas. F. Adams, Jr., | Quincy.    |
| Henry Adams,         | Boston.    |
| Edward Atkinson,     | Boston.    |
| Charles Deane,       | Cambridge. |
| Charles F. Dunbar,   | Cambridge. |
| Samuel Eliot,        | Boston.    |
| George E. Ellis,     | Boston.    |
| Edwin L. Godkin,     | Cambridge. |
| William Gray,        | Boston.    |
| Edward Everett Hale, | Boston.    |
| Henry P. Kidder,     | Boston.    |
| Henry C. Lodge,      | Boston.    |
| Francis Parkman,     | Brookline. |
| Andrew P. Peabody,   | Cambridge. |
| Joseph S. Ropes,     | Boston.    |
| Nathaniel Thayer,    | Boston.    |
| Henry W. Torrey,     | Cambridge. |
| Robert C. Winthrop,  | Boston.    |

## SECTION IV.—13.

*Literature and the Fine Arts.*

|                       |            |
|-----------------------|------------|
| Charles F. Adams,     | Boston.    |
| George S. Boutwell,   | Groton.    |
| J. Elliot Cabot,      | Brookline. |
| Francis J. Child,     | Cambridge. |
| Ralph Waldo Emerson,  | Concord.   |
| Henry W. Longfellow,  | Cambridge. |
| Charles G. Loring,    | Boston.    |
| James Russell Lowell, | Cambridge. |
| Charles Eliot Norton, | Cambridge. |
| Thomas W. Parsons,    | Wayland.   |
| Charles C. Perkins,   | Boston.    |
| H. H. Richardson,     | Brookline. |
| John G. Whittier,     | Amesbury.  |

## ASSOCIATE FELLOWS. — 90.

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## SECTION I. — 8.

*Mathematics.*

Charles Avery, Clinton, N.Y.  
 E. B. Elliott, Washington, D.C.  
 William Ferrel, Washington, D.C.  
 Thomas Hill, Portland, Me.  
 Simon Newcomb, Washington, D.C.  
 H. A. Newton, New Haven, Conn.  
 James E. Oliver, Ithaca, N.Y.  
 T. H. Safford, Williamstown, Mass.

## SECTION II. — 12.

*Practical Astronomy and Geodesy.*

S. Alexander, Princeton, N.J.  
 W. H. C. Bartlett, Yonkers, N.Y.  
 J. H. C. Coffin, Washington, D.C.  
 Wm. H. Emory, Washington, D.C.  
 Asaph Hall, Washington, D.C.  
 J. E. Hilgard, Washington, D.C.  
 George W. Hill, Nyack, N.Y.  
 Elias Loomis, New Haven, Conn.  
 Maria Mitchell, Poughkeepsie, N.Y.  
 C. H. F. Peters, Clinton, N.Y.  
 George M. Searle, New York.  
 Chas. A. Young, Princeton, N.J.

## SECTION III. — 12.

*Physics and Chemistry.*

F. A. P. Barnard, New York.  
 John W. Draper, New York.  
 J. Willard Gibbs, New Haven, Conn.  
 S. W. Johnson, New Haven, Conn.  
 John Le Conte, Berkeley, Cal.  
 A. M. Mayer, Hoboken, N.J.  
 W. A. Norton, New Haven, Conn.  
 Ogden N. Rood, New York.  
 H. A. Rowland, Baltimore.  
 L. M. Rutherford, New York.  
 Benj. Silliman, New Haven, Conn.  
 J. L. Smith, Louisville, Ky.

## SECTION IV. — 6.

*Technology and Engineering.*

Henry L. Abbot, New York.  
 A. A. Humphreys, Washington, D.C.  
 John Rodgers, Washington, D.C.  
 Wm. Sellers, Philadelphia.  
 George Talcott, Albany, N.Y.  
 W. P. Trowbridge, New Haven, Conn.

CLASS II. — *Natural and Physiological Sciences.* — 26.

## SECTION I. — 14.

*Geology, Mineralogy, and Physics of the Globe.*

George J. Brush, New Haven, Conn.  
 James D. Dana, New Haven, Conn.  
 J. W. Dawson, Montreal, Canada.  
 Edward Desor, Neuchâtel, Switz.  
 J. C. Fremont, New York.

F. A. Genth, Philadelphia.  
 Arnold Guyot, Princeton, N.J.  
 James Hall, Albany, N.Y.  
 F. S. Holmes, Charleston, S.C.  
 Clarence King, Washington, D.C.  
 Joseph Le Conte, Berkeley, Cal.  
 J. Peter Lesley, Philadelphia.  
 R. Pumpelly, Newport, R.I.  
 Geo. C. Swallow, Columbia, Mo.

SECTION II.—2.

*Botany.*

A. W. Chapman, Apalachicola, Fla.  
G. Engelmann, St. Louis, Mo.

SECTION III.—9.

*Zoölogy and Physiology.*

S. F. Baird, Washington, D.C.  
J. C. Dalton, New York.  
J. L. Le Conte, Philadelphia.

Joseph Leidy, Philadelphia.  
Leo Lesquereux, Columbus, Ohio.  
O. C. Marsh, New Haven, Conn.  
S. Weir Mitchell, Philadelphia.  
A. S. Packard, Jr., Providence.  
St. Julien Ravenel, Charleston, S.C.

SECTION IV.—1.

*Medicine and Surgery.*

W. A. Hammond, New York.

CLASS III.—*Moral and Political Sciences.*—26.

SECTION I.—8.

*Philosophy and Jurisprudence.*

D. R. Goodwin, Philadelphia.  
R. G. Hazard, Peacedale, R.I.  
Nathaniel Holmes, St. Louis, Mo.  
James McCosh, Princeton, N. J.  
Charles S. Peirce, New York.  
Noah Porter, New Haven, Conn.  
Isaac Ray, Philadelphia.  
Jeremiah Smith, Dover, N.H.

A. D. White, Ithaca, N.Y.  
W. D. Whitney, New Haven, Conn.  
T. D. Woolsey, New Haven, Conn.

SECTION III.—4.

*Political Economy and History.*

Geo. Bancroft, Washington, D.C.  
S. G. Brown, Clinton, N.Y.  
Henry C. Lea, Philadelphia.  
J. H. Trumbull, Hartford, Conn.

SECTION II.—10.

*Philology and Archæology.*

A. N. Arnold, Pawtuxet, R. I.  
D. C. Gilman, Baltimore.  
A. C. Kendrick, Rochester, N.Y.  
Geo. P. Marsh, Rome.  
L. H. Morgan, Rochester, N.Y.  
A. S. Packard, Brunswick, Me.  
E. E. Salisbury, New Haven, Conn.

SECTION IV.—4.

*Literature and the Fine Arts.*

James B. Angell, Ann Arbor, Mich.  
F. E. Church, New York.  
R. S. Greenough, Florence.  
Wm. W. Story, Rome.

## FOREIGN HONORARY MEMBERS.—73.

(Appointed as vacancies occur.)

CLASS I.—*Mathematical and Physical Sciences.*—24.

## SECTION I.—6.

*Mathematics.*

|                     |            |
|---------------------|------------|
| John C. Adams,      | Cambridge. |
| Sir George B. Airy, | Greenwich. |
| Brioschi,           | Milan.     |
| Arthur Cayley,      | Cambridge. |
| Liouville,          | Paris.     |
| J. J. Sylvester,    | Baltimore. |

## SECTION II.—5.

*Practical Astronomy and Geodesy*

|                   |          |
|-------------------|----------|
| Arthur Auwers,    | Berlin.  |
| Döllén,           | Pulkowa. |
| H. A. E. A. Faye, | Paris.   |
| Emile Plantamour, | Geneva.  |
| Otto Struve,      | Pulkowa. |

## SECTION III.—10.

*Physics and Chemistry.*

|                  |             |
|------------------|-------------|
| Berthelot,       | Paris.      |
| R. Bunsen,       | Heidelberg. |
| M. E. Chevreul,  | Paris.      |
| J. Dumas,        | Paris.      |
| H. Helmholtz,    | Berlin.     |
| A. W. Hofmann,   | Berlin.     |
| G. Kirchhoff,    | Berlin.     |
| Balfour Stewart, | Manchester. |
| G. G. Stokes,    | Cambridge.  |
| F. Wöhler,       | Göttingen.  |

## SECTION IV.—3.

*Technology and Engineering.*

|                   |          |
|-------------------|----------|
| R. Clausius,      | Bonn.    |
| F. M. de Lesseps, | Paris.   |
| Sir Wm. Thomson,  | Glasgow. |

CLASS II.—*Natural and Physiological Sciences.*—27.

## SECTION I.—7.

*Geology, Mineralogy, and Physics of the Globe.*

|                       |             |
|-----------------------|-------------|
| Barrande,             | Prague.     |
| Charles Darwin,       | Beckenham.  |
| Des Cloizeaux,        | Paris.      |
| James Prescott Joule, | Manchester. |
| C. F. Rammelsberg,    | Berlin.     |
| A. C. Ramsay,         | London.     |
| Sir Edward Sabine,    | London.     |

## SECTION II.—7.

*Botany.*

|                       |         |
|-----------------------|---------|
| J. G. Agardh,         | Lund.   |
| George Bentham,       | London. |
| Alphonse de Candolle, | Geneva. |
| Decaisne,             | Paris.  |
| Oswald Heer,          | Zurich. |
| Sir Joseph D. Hooker, | London. |
| Nägeli,               | Munich. |

## SECTION III.—9.

*Zoölogy and Physiology.*

|                     |           |
|---------------------|-----------|
| T. L. W. Bischoff,  | Munich.   |
| Milne Edwards,      | Paris.    |
| Albrecht Kölliker,  | Würzburg. |
| Rudolph Leuckart,   | Leipsic.  |
| Richard Owen,       | London.   |
| Theodor Schwann,    | Liége.    |
| C. Th. von Siebold, | Munich.   |

|                      |             |
|----------------------|-------------|
| J. J. S. Steenstrup, | Copenhagen. |
| Valentin,            | Berne.      |

## SECTION IV.—4.

*Medicine and Surgery.*

|                      |          |
|----------------------|----------|
| C. E. Brown-Séquard, | Paris.   |
| F. C. Donders,       | Utrecht. |
| Sir James Paget,     | London.  |
| Virchow,             | Berlin.  |

CLASS III.—*Moral and Political Sciences.*—22.

## SECTION I.—4.

*Philosophy and Jurisprudence.*

|                         |             |
|-------------------------|-------------|
| J. C. Bluntschli,       | Heidelberg. |
| Sir Henry Sumner Maine, | London.     |
| James Martineau,        | London.     |
| Sir James F. Stephen,   | London.     |

## SECTION II.—7.

*Philology and Archæology.*

|                      |            |
|----------------------|------------|
| Georg Curtius,       | Leipsic.   |
| Pascual de Gayangos, | Madrid.    |
| Benjamin Jowett,     | Oxford.    |
| Lepsius,             | Berlin.    |
| Max Müller,          | Oxford.    |
| H. A. J. Munro,      | Cambridge. |
| Sir H. C. Rawlinson, | London.    |

## SECTION III.—8.

*Political Economy and History.*

|                     |         |
|---------------------|---------|
| Ernst Curtius,      | Berlin. |
| W. Ewart Gladstone, | London. |
| Charles Merivale,   | Ely.    |
| F. A. A. Mignet,    | Paris.  |
| Mommsen,            | Berlin. |
| Mark Pattison,      | Oxford. |
| Von Ranke,          | Berlin. |
| A. P. Stanley,      | London. |

## SECTION IV.—3.

*Literature and the Fine Arts.*

|                  |                |
|------------------|----------------|
| Gérôme,          | Paris.         |
| John Ruskin,     | Coniston.      |
| Alfred Tennyson, | Isle of Wight. |





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